

Design and Development of Electrochemical Cell for Converting Carbon Dioxide to
Useful Fuel

by

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ABSTRACT

The majority of the natural issues the world is confronting today is because of our dependence on fossil fuels and the increase in CO₂ emissions. The alternative solution for this problem is the use of renewable energy for the energy production, but these are uncertain energy sources. So, the combination of reducing carbon dioxide with the use of renewable energy sources is the finest way to mitigate this problem. Electrochemical reduction of carbon dioxide (ERC) is a reasonable approach as it eliminates as well as utilizes the carbon dioxide as a source for generating valuable products.

In this study, development of electrochemical reactor, characterization of membrane electrode assembly (MEA) and analysis of electrochemical reduction of carbon dioxide (ERC) is discussed. Electrodes using various catalyst materials in solid polymer based electrolyte (SPE) along with gas diffusion layer (GDL) are developed. The prepared membrane electrodes are characterized under ex-situ conditions using scanning electron microscopy (SEM). The membranes are later placed in the electrochemical reactor for the in-situ characterization to assess the performance of the membrane electrode assembly.

The electrodes are processed by airbrushing the metal particles on the nafion membrane and then are electrochemically characterized by linear sweep voltammetry. The anode was kept constant with platinum whereas the cathode was examined with compositions of different metal catalysts. The products formed subsequently are analyzed using gas chromatography (GC) and Residual gas analysis (RGA). Hydrogen (H₂) and carbon monoxide (CO) are detected using GC while the hydrocarbons are detected by performing quantitative analysis using RGA. The preliminary experiments gave very encouraging results. However, more work needs to be done to achieve new heights.

DEDICATION

This thesis is dedicated to my parents, Venka Saibabu and Venka Laxmi babu who have provided me with moral support and guidance throughout my academic career. This is not possible without their constant love, affection and belief in me.

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1 INTRODUCTION

1.1 Effects of CO₂ on Climate Change

The intensification of growing population and human industrial activities are destroying the world's natural resources. To supply energy for the future generations has become the biggest challenge for the scientists. According to the BP statistical review 2015 ("Bp-Statistical-Review-of-World-Energy-2015-Full-Report.pdf..pdf" 2016), the primary world energy consumption increased to 12.9 K million tonnes oil equivalent which is 1% increase when compared 2014 to 2013 data. The non- OECD (non- organization for economic growth and development) countries accounts for highest consumption of total growth which is 57.5 %. On April 19 2016 National Oceanic and Atmospheric Administration (NOAA) has stated that the globe was recorded warm for 11th straight month ("For 11th Straight Month, the Globe Was Record Warm | National Oceanic and Atmospheric Administration" 2016). The earth's temperature is warm due to the burning of fossil fuels and they are largely because of the human behavior. The use of fossil fuels without any care to run the vehicles, power factories and others releases the CO₂ stored for millions of years ago as oil, coal. In the last 200 years' large amounts of these have been burned resulting in increased amounts of CO₂ in the atmosphere. This increase in CO₂ in the atmosphere thickens the greenhouse blanket which leads to trapping the heat into the earth's atmosphere. Thus upsetting a delicate balance and causing global warming and the rise in global temperature. The increasing amounts of carbon dioxide present in the atmosphere -29 billion tonnes of it as recorded till 2014 warms up the globe as stated by world wide fund (WWF) in 2015 ("Climate & Energy" 2016). The increase of CO₂ levels in the atmosphere in recent years is shown in figure 1. The data have been

taped at the Mauna Loa since pre industrial times. The value of 280 ppm is close to the measured average of CO₂ so it has been chosen as representative of pre-industrial air and is logged in with accuracy in time between the years 1000 and 1800 in an ice core from Law Dome, Antarctica (Etheridge et al. 1996). The atmospheric CO₂ is expressed both in ppm and as a percentage change since 1800. After the water vapor has been removed, the Data reported as dry air mole fraction, which means number of molecules of CO₂ divided by number of molecules in air. The mole fraction is expressed as parts per million (ppm).

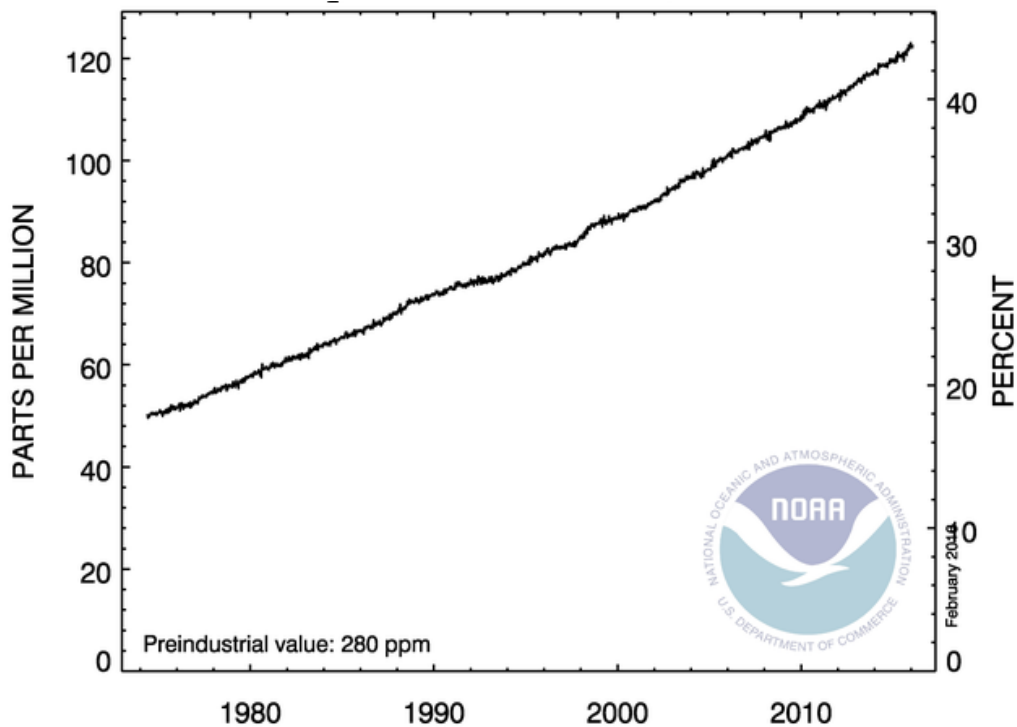


Fig 1: Atmospheric Carbon Dioxide Levels in Recent Years.

Photo Courtesy: (US Department of Commerce 2016)

Rise in level of CO₂ in the atmosphere is directly related to the rise in global temperature. The consequences of rise in global temperature would be more frequent wildfires, droughts for a long time in few regions which effects the agriculture, rise in natural

disasters, humans and animal's health, noticeable effects on the environment. Scientists predict that the rise in global temperature continue to rise, mainly because of the emission of greenhouse gases. Union of concerned scientists have recently published an article regarding why CO₂ gets most of the attention compared with other greenhouse gasses ("Global Warming" 2016). Firstly, because it puts us at a greater risk of irreversible changes if it continues to increase in the atmosphere as most of the global warming happening is due to CO₂ and its influence is expected to continue. The other reason is CO₂ sticks in the atmosphere longer compared to any other greenhouse gasses. But to get rid of methane emissions present in the atmosphere it would take about 10 years, which in turn is going to convert into CO₂, while nitrous oxide will take about a century. The CO₂ emissions present as of today would take about a century to leave but 20 percent of it is still going to stay in the atmosphere for about 800 years from now. CO₂'s long life in the atmosphere makes it a strong reason for us to reduce their emissions as early as possible.

The other major question which pops up is if CO₂ constitutes to a minute portion to the atmosphere how can it be the main reason behind global warming and how can such less quantity lead to such massive effects. Pieter Tans, a senior scientist at the NOAA earth system research laboratory has given an answer ("If Carbon Dioxide Makes up Only a Minute Portion of the Atmosphere, How Can Global Warming Be Traced to It? And How Can Such a Tiny Amount of Change Produce Such Large Effects?" 2016). The visible radiation from the sun is absorbed by the earth surface thus heating takes place. Simultaneously the surface and the atmosphere emit the infrared rays back to the space thus cooling takes place. The earth's surface temperature is going to be constant as long

as this balance is maintained. Due to this increase in greenhouse gasses the infrared rays emitting back to the atmosphere are slightly lower than those absorbing thus increasing the temperature of the surface. This excess energy will warm up the oceans, though it takes a very long time to heat up but when they will, they emit infrared rays to the space but lack of thick layer of greenhouse gasses available in the atmosphere the planet will continue to stay warmer. The scientists are expecting that the earth's temperature would increase by 0.5 percent considering the CO₂ emissions would stop increasing at the very moment which is not the case as we continue to burn coal, natural gas for our increasing needs.

1.2 CO₂ Utilization and Conversion

CO₂ utilization mainly focuses on peculiar ways to reduce carbon dioxide emissions by finding out the uses of CO₂ that will help in diminishing CO₂ emissions in places where storing is not a best solution. CO₂ if used appropriately can have many benefits. There are many approaches coming up to capture CO₂ or to convert it to useful products such as chemicals, fuels, cements and plastics. Every potential use of CO₂ requires energy that has to be determined, and the CO₂ produced to provide the energy for some specific utilization process should not exceed the CO₂ utilized. In a recent article published in smart specialization platform by the European commission have mentioned that CO₂ utilization may delay their emissions into the atmosphere while reducing the consumption and avoiding the emissions from other sources. Enhanced oil and gas recovery which stands for EOR and EGR, CO₂ mineralization can be stored permanently whereas in the other utilization processes the emissions are delayed into the product chain.

The alternative to the CO₂ storage is the CO₂ capture and utilization due to its potential.

The market predictions were made is around 200 Mt CO₂ /y (Aresta, Dibenedetto, and Angelini 2013) when compared to 14,000 Mt CO₂ /y which were emitted from a large source (Boot-Handford et al. 2014). CO₂ utilization market is really small and further markets should also prioritize CO₂ emissions with their utilization (“Accelerating the Uptake of CCS: Industrial Use of Captured Carbon Dioxide | Global Carbon Capture and Storage Institute” 2016). As per Bio- based news 2015 (“Sustainable Fuels, Chemicals and Polymers from Sun and CO₂ - Bio-Based News - The Portal for Bio-Based Economy and Industrial Biotechnology” 2015), the carbon capture and utilization is gaining momentum and their uses in the industry sector is going to be the future. There are many applications in terms of their processes and uses. The figure 2 depicts the current and potential uses of captured CO₂, but many of them are used in small scale and they usually emit CO₂ to atmosphere, thus resulting in no reduction in overall CO₂ emissions.

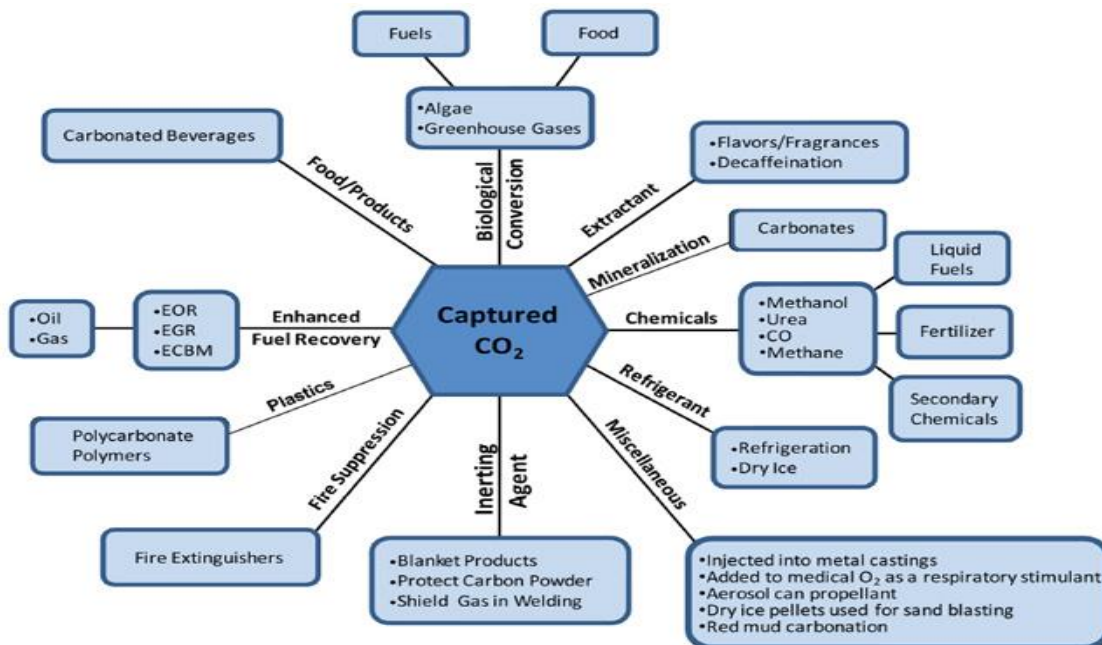


Fig 2: Classification of CO₂ Utilization

Photo Courtesy: (“CO₂-Utilization | Netl.doe.gov” 2016)

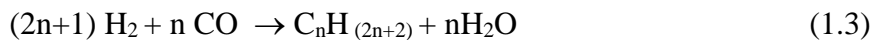
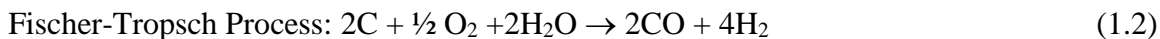
As our primary energy source i.e. fossil fuels are depleting, renewable energy sources such as solar, wind, nuclear, geothermal, biomass etc. will take its place. But these sources alone cannot meet the requirements unless if they are stored so that they can be used whenever it is necessary independent of when there is sunlight or when the wind is blowing. We can store the energy produced by renewable sources through few technologies. One way is to do mechanically by the use of a flywheel- in which energy is stored through rotation. Secondly, it can be stored with the help of batteries, but energy densities obtained are lower compared to that of the primary sources. Thirdly to store it electrochemically, where the energy is used to run through chemical reactions and store it in the form of products formed. As we know that there is rise in carbon dioxide percentage in the atmosphere, we can reduce carbon dioxide electrochemically to form some reaction products with the help of renewable energy. It is proven that CO₂ can be reduced to many high energy density products.

The conversion of CO₂ to useful fuel is carried out by two process. The first process is called the Sabatier process and the next process is called the Fischer-Tropsch process. The first process was discovered by the French chemist Paul Sabatier which involves the reaction of hydrogen and carbon dioxide at high temperatures and pressures with help of nickel catalyst to produce methane and water. Equation (1.1) shows a clear depiction of this conversion of hydrogen and CO₂ to methane and water.



The Fischer-Tropsch process is developed by Franz Fischer and Hans Tropsch which consists series of chemical reactions that converts carbon monoxide and hydrogen into liquid hydrocarbons, having the formula as (C_nH_(2n+2)). Equation (1.2) and equation (1.3)

depicts the Fischer-Tropsch reaction mechanism.



Where n ranges from 10-20. Methane forms when $n=1$ which is not necessary. Many processes like photochemical, biochemical, electrochemical and so on, are being studied in order to obtain hydrocarbons by utilizing CO_2 . However most of these methods require high temperatures or high pressures or both to obtain a product. Yet, they produce low product. So the concentration on the research of electrochemical method has been increased due to its advantages over other techniques because of their simplicity, reactions occurring at ambient conditions and many others which would be discussed further.

1.3 Prospects and Challenges of ERC

Lately the research has shown that by reducing carbon dioxide electrochemically can produce various organic compounds like formic acid, methane, carbon monoxide, hydrogen and others with high current efficiency. Electrochemical reduction of carbon dioxide in recent years have won over other technologies due to its advantages. They are:

- It reduces harmful CO_2 from the atmosphere to useful products.
- It forms fuels or the hydrocarbons especially, CH_4 , C_2H_6 , CH_3OH etc.
- The electrochemically reduced CO_2 used as a feedstock for various chemicals.
- It can store the energy coming from the renewable sources, and can be used whenever it's necessary instead of waiting when they will be available.
- The whole process is run at ambient conditions, without creating any complexities.

- This setup can be scaled up to any size easily, thus meeting the requirements of the respective industries.

The challenges that we face while reducing CO₂ are:

- Transportation of CO₂ to the reaction system.
- Minimize the catalyst from corroding and poisoning.
- To increase the current densities and to achieve high efficiencies.
- To collect the products effectively from the outlet without any wastages.
- It is important to find new reaction paths and catalysts to produce new products.
- To analyze and separation of the products obtained.
- Increasing the faradaic efficiency to increase the energy efficiency and reducing the over potential of the reactions taking place.
- Collecting the products from catalyst layer without blocking the catalyst active site.

1.4 Objectives

The main objectives of this study are:

- i. To design and develop a system prototype for reducing CO₂ in a solid polymer electrolyte based electrochemical reactor.
- ii. Understand the significance of solid polymer electrolyte in electrochemical reduction of CO₂ to useful products.
- iii. Design an electrochemical reactor to perform the reduction of gaseous CO₂.
- iv. Analyze the reaction products for compositions of various useful products.

1.5 Thesis Layout

Chapter 2 provides a literature review of past studies on electrochemical reduction of carbon dioxide. It includes different ways to reduce to carbon dioxide and the CO/CO₂ hydrogenation. A brief study on various electrolytes, electrode materials, operating conditions and the products formed. Discussions are made on the use of liquid electrolytes and the introduction of solid polymer based electrolyte and their effect on the performance. It is also mentioned how the changing in electrolyte, electrode and operating conditions effect the products formed.

Chapter 3 details the experimental design, mechanism, including material properties, proportions, mixing procedures, fabrication of the electrodes and the membrane electrode assembly, gas diffusion layer and nafion electrolyte have also been discussed and test methods used to assess the performance of the ERC reactor.

Chapter 4 discusses the characterization techniques of the membranes as well as the performance of the membrane within the reactor. Ex-situ methods like Scanning electron microscopy has been used to characterize the membrane. In- situ methods have also been studied.

Chapter 5 is devoted to understanding the products formed by reducing carbon dioxide in electrochemical reactor using gas chromatography and residual gas analysis. Gas chromatography with TCD detector has been used. RGA is used to perform quantitative analysis to identify the products that are formed.

Chapter 6 provides a detailed conclusion of the studies carried out on using different catalyst materials in the electrochemical reactor and future recommendations have also been made.

2 LITERATURE REVIEW

This chapter contains comprehensive literature survey with prominence on recent advancements for electrochemical reduction of carbon dioxide.

2.1 CO₂ Reduction

Studies on different pathways to convert carbon dioxide to hydrocarbons and alcohols have been done by the researchers. Hydrogenation of carbon dioxide has shown encouraging results in pilot plants but the process is less efficient because of the high temperatures and pressures along with high consumption of hydrogen. Hence, reduction process taking place at ambient conditions in addition using renewable energy like solar energy or electrical energy are more economical and attractive routes. In 2008, Hori has developed the conversion of carbon dioxide via aqueous electrocatalytic reduction (Y. Hori 2008).

2.2 CO/CO₂ Hydrogenation

Over a century, efforts are taking place to convert carbon dioxide to hydrocarbons. As discussed earlier Franz Fischer and Hans Tropsch invented the Fischer- Tropsch process in 1920 (“Fischer–Tropsch Process” 2016). It mainly consists of two main steps, the first is the partial oxidation of natural gas to hydrogen gas and CO₂. These products are later converted into formic acid, ethanol, methanol etc. Methanol is usually produced from synthetic gas which is a combination of CO, H₂ and traces of CO₂. Equation (2.1) depicts the combination of synthetic gas explained by a stoichiometric number S.

$$S = \frac{molH_2 - molCO_2}{molCO + molCO_2} \quad (2.1)$$

For methanol formation S is slightly below 2. Presence of CO₂ will lower the S value and

presence of H₂ increases the S value. The lower the value of S, higher the productivity. The studies have shown that when carbon dioxide and carbon monoxide when mixed in proper quantities increases the methanol concentration and also decreases the activation energy of the reaction (Klier et al. 1982; King and Nix 1996; J. S. Lee et al. 1993). Although many different catalyst combinations have been studied over past few years, copper – zinc oxides along with various promoters for example ZrO₂, SiO₂ and Ga₂O₃ are few important among various other promoters (Yee, Zhang, and Ladewig 2013). To achieve a fuel like methanol using copper based catalysts is a surface sensitive reaction and the catalyst surface structure and stability will decide the activity and selectivity of the product. Among the many products formed from copper based catalysts methanol is the highly formed products as mentioned by several researchers' (Jingfa et al. 1996; Pan et al. 1988; Rasmussen et al. 1994). (Chinchen, Waugh, and Whan 1986) claimed that the product formation is independent of copper surface area while Herman (Herman et al. 1979) claim that the Cu⁺ are responsible for the product formation. (Szanyi and Goodman 1991) declared that oxidization of copper particles will lead to higher formation of the products.

In near future renewable energy should replace fossil fuels, non-renewable energy sources. Various emissions and the atmosphere will have the necessary amounts of carbon dioxide required for conversion. By getting back the fossil fuels and carbon dioxide from air will give us sufficient amount of carbon dioxide for hydrogenation. There are few drawbacks with the hydrogenation procedure, like it requires high energy to generate hydrogen. It is not a difficult act to capture carbon dioxide compared to forming hydrogen. The other method to produce hydrogen is water electrolysis. In this

process electrodes are immersed in water and an electric current is applied between these electrodes, but the drawback here is it requires more hydrogen than the products hydrocarbons and alcohols are consumed. To mitigate these difficulties there are other ways we can consider like, electrochemical reduction of CO₂. By performing these methods, we can obtain hydrogen, carbon monoxide, formic acid, methane and methanol at ambient conditions and high selectivity.

2.3 Electrochemical Reduction of Carbon Dioxide

The relationship between chemical reactions and electricity was investigated by Galvani and Volta in the late 18th century (“MEET GALVANI and VOLTA” 2016). When externally applied voltage drives the reaction or voltage is created by a chemical reaction, it is termed as an electrochemical reaction. Electrochemical is the study of chemical reactions occurring at the interface of electrode and electrolyte. The electrons transfer from electrode to the electrolyte. These are also called as redox reactions due to transfer of the electrons.

Several authors have found out many different ways for the conversion of carbon dioxide into useful products. At various temperatures and pressures experiments were performed and in addition using solar energy is the most striking ways to conduct this reduction process. Hydrogen, formic acid, methane, carbon monoxide, methanol and ethanol are the most commonly formed products of the electrochemical reduction of CO₂ on metal electrodes. However, the efficiency and the rate of formation is quite low. Many of the researchers have reduced CO₂ using the liquid electrolyte, but using a solid polymer electrolyte will mitigate material handling problems and simplifies the process and it can be modified according to our needs. However, solid polymer electrolyte when used in

this reduction process has to meet few basic requirements. They are:

- High ionic conductivity
- Electrochemically and thermally stable
- Possess good tensile strength
- Good mechanical properties
- Economical and Easy to manufacture
- It should be made practically possible and easy to scale up
- It should be reliable and lasting

The effects of electrolytes, catalyst, experimental parameters, pH, conductivity of the electrolyte, voltage applied and products formed along with their efficiencies have been discussed by many researchers and the summary is described in Table 2.1. The conversion of ERC to useful products mainly depends on the catalyst materials, the reaction medium and operating conditions. On analyzing the table, we can figure out that changing the electrode and the electrolyte composition the output product varies. It is also noted that most of the researches are conducted using liquid electrolyte like aqueous bicarbonate solutions with metal catalysts like Copper, Platinum, combinations of copper and zinc, lead, Tin etc. Operating temperatures also have an impact on the products formed. It is noted that the common byproduct formed is usually formic acid, which is the simplest carboxyl acid and occurs naturally. The main use of formic acid, it acts as a preservative in livestock feed. But, the interests and the challenge lies in reducing the CO₂ to hydrocarbons. Studies on various catalyst combinations and procedures have been discussed over past few years, among which copper and copper-zinc oxides along with

few promoters are considered to be the main catalysts (Liu et al. 2003). With the help of these catalyst CO₂ can be electrochemically reduced to many useful products as discussed earlier. As copper based catalysts are highly surface sensitive, the activity and selectivity strongly depend on the catalyst's surface structure and stability. It is also said that as the area of the catalyst increases, the catalyst activity also increases (Askgaard et al. 1995; Pan et al. 1988; Rasmussen et al. 1994).

Table 1: Studies on Various Parameters for Electrochemical Reduction of CO₂

Electrode	Electrolyte	Operating Conditions	Main Products (Faradaic Efficiency %)	References
Indium	NaHCO ₃	pH=8,40 mA.cm ⁻²	Formate(45)	(Narayanan et al. 2011)
CuBr	3M KBr	46.1 mA.cm ⁻² , pH=3	C ₂ H ₄ (80) ; H ₂ (9)	(H. Yano et al. 2004)
Cu foil	0.1 M KHCO ₃	10 mA.cm ⁻²	CH ₃ OH (0.1)	(Kuhl et al. 2012)
Lead	NaOH	2.5 mA.cm ⁻² ,pH =8.5	Formate(70)	(Innocent et al. 2008)
Cu ₂ O-ZnO	0.5 M KHCO ₃	-1.8V vs. Ag/AgCl	CH ₃ OH (25.2)	(Albo et al. 2015)
Cu mesh	0.1 MKHCO ₃	14.78 cm ³ min ⁻¹	C ₂ H ₄ (10.7); C ₂ H ₆ (3.7)	(Gonçalves et al. 2010)
Cu foil	0.5 M KHCO ₃	(-)1.85 V	CH ₄ (31); C ₂ H ₄ (10); CO (3)	(Kyriacou and Anagnostopoulos 1993)
Cu foil	0.5 M KHCO ₃	30–35mAcm ⁻² at -2.00V	CH ₄ -C ₂ H ₄ (64)	(Dewulf and Bard 1988)
Cu ₂ O/Zn	KOH/methanol	243K, pH=7.5	CH ₄ (7.5) ; C ₂ H ₄ (28)	(J. Yano and Yamasaki 2008)
Cu	0.45M KHCO ₃	22 mA.cm ⁻² , 298K	Formate (86)	(Y. Hori et al. 2005)

Electrochemical reduction of CO₂ on copper electrodes is usually performed in KHCO₃ electrolyte solutions by various researchers (Kyriacou and Anagnostopoulos 1993; Y. Hori et al. 2005; Yoshio Hori et al. 1986; Kaneco et al. 2003). The output obtained when electrochemical reduction of CO₂ on copper in bicarbonate electrolyte solution is ethylene, which was flattering because it reduced the bicarbonate concentration and increased the pH at the electrode surface which in turn decreased the methane to ethylene ratio (Murata and Hori 1991). When the copper electrodes were in presence of KCl electrolyte solutions, there was not much effect on the decrease in bicarbonate concentration and as well as on the methane to ethylene ratio as there was high pH value at the electrode surface in KCl solutions in comparison to KHCO₃⁻. After performing several tests with Cu/PTFE GDE in various concentrations of potassium bicarbonate electrolyte, (K.-R. Lee et al. 1999) Lee in 1999 presented that methane to ethylene ration reduces with increase in HCO₃⁻ and pH increases on the electrode surface. It is noted that the evolvement of methane decreases in the order of Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺. With the addition of promoters such as potassium hydroxide ethylene evolution is tending to be higher in methanol, whereas methane evolution is tending to be higher in methanol with addition of sodium and lithium perchlorate. It is also observed that hydrogen evolution decreases with decrease in the cationic size in the aqueous solutions.

Various treatments have been done on copper , (Terunuma, Saitoh, and Momose 1997) to study the interconnection between the evolution of hydrocarbons and attributes of cooper as an electrode. As mentioned earlier, since the copper surfaces are very sensitive and have high compatibility with oxygen they get easily poisoned with organic compounds. (“Thesis.pdf” 2016). It was observed initially that the copper surface was the solo reason

for the reduction of carbon dioxide into CO and Cu₂O was preferred over Cu because the adsorption was found higher. Gas diffusion electrode coated with copper was acquainted by Ikeda in 1995 (Ikeda et al. 1996). The products formed were CH₄, C₂H₆, C₂H₅OH, CO and HCOO⁻. It was observed that the faradaic efficiencies obtained were less compared to those that were formed with Cu₂O electrodes. It was reported by Goncalves (Gonçalves et al. 2010) that ethylene was formed when copper deposits were found on the cathode in the reduction process of CO₂. From the observations, it was stated that the ethylene evolution increases with increase in the surface area of the copper deposits on the cathode i.e. from 18.7% to 33%. Experiments were also conducted by positioning platinum near the CO₂ which forms methane with a faradaic efficiency of 38.8%, it was noted that the methane evolution increases with the increase in pressure with a peak limit of 20 atm.

When CO₂ is electrochemically reduced off with the use of copper oxide as the catalyst the main product identified is methanol (Chang et al. 2009a). It is said that the cuprous oxide improves the stability of the intermediate products which plays a major role in the formation of methanol (Le et al. 2011). Methanol evolution is 43 μmol.cm⁻².h⁻¹ and faradaic efficiency 38% which is considered to be the highest. In methanol formation metal catalysts are usually added to improve the yield and activity and zinc has been added to the copper oxide to improve the process. (Herman et al. 1979) Herman et al., 1979 manifested that ERC using copper electrode yielded just 10⁻⁸ kg of methanol per m² hour, but when metal catalyst zinc is added to the copper there was an increase in the methanol evolution i.e. 3.63 x 10⁻⁵ kg of methanol per m² hour.

(Karl W. Frese 1991) Frese has first revealed that the electrochemical reduction of carbon dioxide to CH₃OH in aqueous electrolytes using GaAs and InP semiconductor electrodes,

but the maximum current densities it could reach was less than 1mA cm^{-2} as reported by Canfield et al., 1983. Carbon dioxide is reduced on various types of Mo (Summers, Leach, and Frese 1986) and Ru electrodes (K. W. Frese and Leach 1985; Bandi 1990; Qu et al. 2005) with Faradaic efficiencies upto 60% and current density less than 2mA cm^{-2} . We should also consider that Faradaic efficiencies depend on 6-electron reduction process and if the efficiency is more than 100% it denotes that they are electrochemical-chemical mechanisms.

However, the electrode stability and the oxidation state are not taken into account, Copper oxide showed phenomenal response towards electrochemical reduction of carbon dioxide. But a more stable catalyst is required for high selectivity because copper oxide corrodes in a simultaneous reactions and the experiments could not be repetitive with the same electrode. As we have already seen many researches working with copper oxide and getting encouraging results, it would make more sense to stabilize the copper oxide surfaces. Wilmer in 2003 (Wilmer et al. 2003) has recognized few particles of ZnO are actively involved in the formation of methanol and as we know electrochemical reduction of CO_2 is surface sensitive, using ZnO along with Cu_2O would be suitable option.

Numerous researches has been done on copper or copper foils, copper meshes and many other copper derived electrodes. The faradaic efficiencies of the formation of various hydrocarbon products are significantly low, which means vast improvement has to be done. In order to enhance the performance and to mitigate the aqueous solutions problems, solid polymer electrolyte (SPE) has been proposed into the electrochemical reduction of CO_2 process. Nonetheless, the advancement in this process is still finite and enough work has to be done to substantiate solid polymer electrolyte in ERC.

3 EXPERIMENTAL

This chapter contains the description of the mechanism, construction of the electrochemical setup, fabrication of electrodes and assembly of membrane electrode assembly and the electrochemical technique involved for research in this thesis.

3.1 Mechanism

In electrochemical reactor the reduction of CO_2 allows you to convert Carbon dioxide and water into useful products using renewable energy. This process of reducing CO_2 using renewable energy can also be called as artificial photosynthesis by Wilcox in 2012 (Wilcox 2012), as it converts solar energy to carbon based fuels. As we know, CO_2 is a well-balanced particle so it requires large amount of energy to run this process. Kobayashi and Tanaka in 2014 have reported that CO_2^- is the rate determining step in the reduction process (Kobayashi and Tanaka 2014) . The potential voltage for CO_2^- is -1.9 vs. SHE (standard hydrogen electrode), to obtain this high energy is reduced by the proton accelerated electron reduction of CO_2 . The underlying principle behind electrochemical reduction process is discussed below.

An electrochemical cell is a mechanism which generates electrical energy from chemical reactions. It consists of two half cells, one has an electrolyte and the other has an electrode. In these cells, one kind in the half cell loses electrons to the electrode and gets oxidized while the other gains electrons from their electrode and reduction occurs. Difference in charge occurs when there is flow of electrons from one half cell to the other and this charge further helps the electrons to flow freely. There are two different kinds of electrochemical cells, the first is galvanic cell, the conversion of chemical energy into electrical energy occurs spontaneously. Second is electrolytic cell, it is a non-spontaneous

reaction which requires electrical energy to convert the reactants into products. The illustration of the electrochemical cell mechanism is depicted in the figure 3. As shown in the illustration the electrochemical cell has two electrodes-cathode and anode, electrolyte, input valves and the output valves.

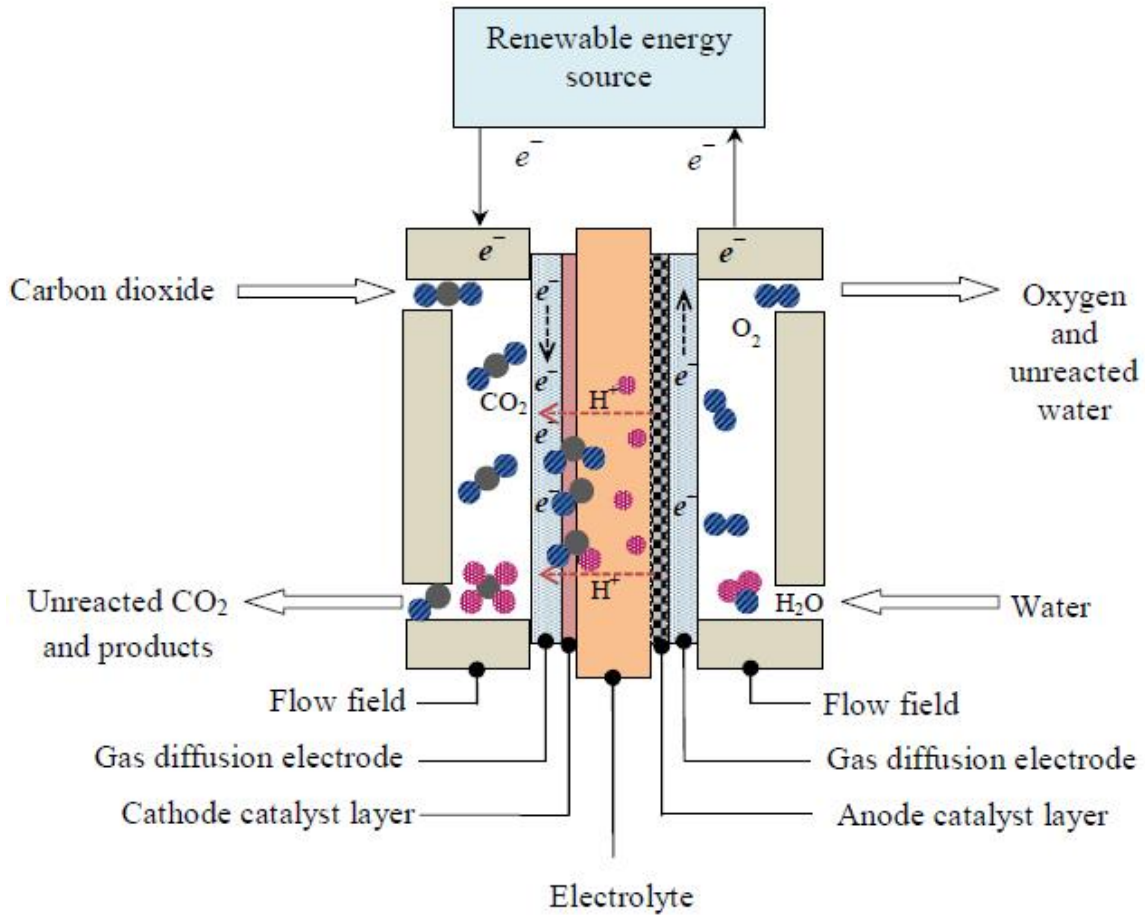
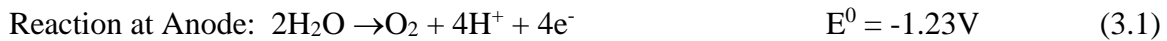


Fig 3: Illustration of an Electrochemical Cell for the Reduction of CO₂ (Aeshala, Rahman, and Verma 2011).

Renewable energy drives the cell by reducing the carbon dioxide at the cathode and oxidizing the water at anode. The oxidation of water at an applied voltage of 1.23V is shown in the Equation 3.1. The reactants formed are oxygen, electrons and protons. The

electrodes formed at anode are sent to the cathode through the external circuit. The reduction of CO₂ is occurred at anode and it is shown in the equation 3.2. The electrons and protons from the anode transported to the cathode react with the CO₂ and the output formed is CH₄ as shown in the equation 3.2. The electrolyte which is in between the cathode and the anode act as a separator between carbon dioxide and water to make sure that they don't mix and helps to complete the external circuit through which electrons and protons are carried from anode to cathode. The total reaction is shown in the equation 3.3.



As we can see from the equation 3.2 the potential is positive which means it is a feasible reaction at the cathode as the major part of the energy is used at the anode. From the total reaction it can be concluded that at atmospheric conditions one mole of carbon dioxide generates one mole of methane when a voltage of -1.06V is applied.

3.2 Construction of Electrochemical Reactor

Electrochemical cell was manufactured and developed to learn the performance of the catalyst and the membrane in the practical world. ERC is assembled with two graphite plates with flow channels which helps in liberating the reacting materials at anode and cathode. These graphite plates are fastened to the monopolar plates also called as the end plates which helps in holding the total cell together. The end plates have four channels, two for the inlet and two for the outlet. Figure 3.1 shows the whole assembly of the cell. The input channel on the cathode side is connected to the carbon dioxide while the input on the anode side is connected to the peristaltic pump which pumps the water to the cell.

The output channel on the cathode side is to collect the excess water, while that on the anode is to collect the products. The Red, black, green and gray terminals are connected to PARSTAT 2273 which supplies the electrical potential to the cell. The electrons and protons formed at the anode side are compiled by the end plate at the anode, which are allowed to flow through the terminals attached and are transported to the cathode side through the external circuit and then reach the end plates of the cathode side. The membrane electrode assembly is placed in between the two graphite plates. The end plates seal the whole cell. As seen in figure the rubber sleeves are used to insulate the cell from short circuiting. Thus the cell has been completely assembled.

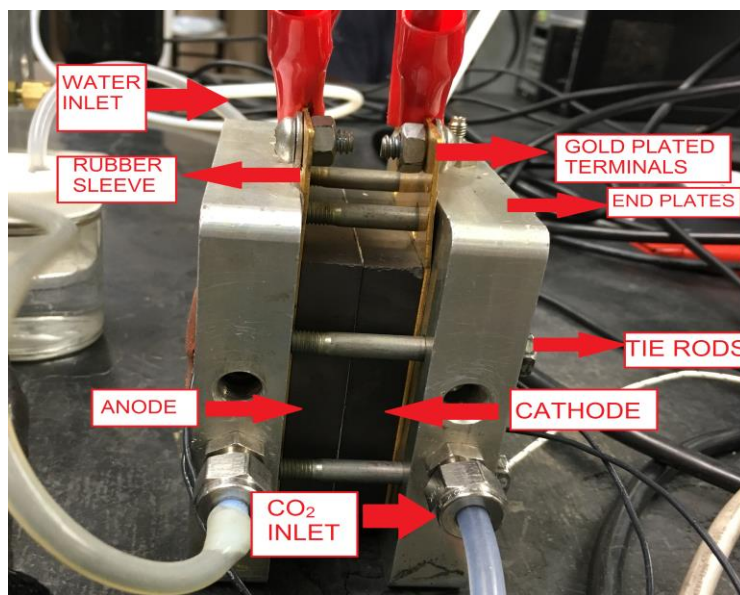


Fig 4: Electrochemical Reactor

3.3 Preparation of Membrane Electrode Assembly

Anode and cathode catalysts need a support in the ERC cell. This support is given by a porous carbon paper also called as gas diffusion layer (GDL). Hollingsworth & Vose Company's carbon paper has been used from Massachusetts, USA. The electrical contact

between the catalyst and current collector is provided by the GDL. An ink is coated or sprayed on the porous carbon paper to increase the electrical conductivity. The ink is made up of pure black and vapor grown carbon fiber (VGCF) in the ratio of 75% and 25%. After they are mixed well, sodium dodecyl sulfate (SDS) is added along with distilled water. Sonicate it for half an hour followed by stirring for about an hour. Then add polytetrafluoroethylene (PTFE) into the mixture and continue stirring for 10 minutes. Use this ink to coat or spray on the carbon paper and dry the sample overnight at room temperature. Then sinter the sample at high temperature for half an hour and wash it with distilled water and dry the sample for a day. The gas diffusion layer is ready to use.

The electrodes are formed by depositing a thin catalyst layer on the nafion membrane (Nafion 212) with the help of a spray gun. The anode catalyst layer is formed by making a slurry with 40 wt. % Pt/C catalyst and by mixing IPA (isopropyl alcohol) and the nafion dispersion and then sonicating it for about 20 minutes. The loading of the catalyst at the anode is 0.5 mg.cm^{-2} . The anode is formed by heat treating in the oven at 100°C for half a day. The cathode layer is formed by spraying the catalyst of various materials and different loadings ranging from 0.5 mg/cm^2 to 2 mg.cm^2 . The materials that have been tested were platinum, copper oxide, copper oxide/ zinc oxide, lanthanum copper oxide. Most of the research was done using Cu_2O and $\text{Cu}_2\text{O}/\text{ZnO}$ mixed particular ratio. The Cu_2O electrodes were prepared by airbrushing the catalyst ink on the nafion surface. This catalyst ink is a mixture of Cu_2O particles bought from sigma Aldrich of particle size $<350\text{nm}$ which is dispersed in 1.5% (w/v) in ethanol as electrocatalyst, nafion dispersion of 5 %wt. acts as a binder and isopropanol acts as a vehicle for the 70:30 ratio of catalyst/nafion mass ratio. This mixture is allowed to sonicate for 15 min. The Cu_2O

electrodes of various catalyst loadings, L, were prepared by simple collection of layers and IPA evaporation. The ZnO particles are bought from sigma Aldrich of particle size <100nm and 5wt % in H₂O. The Cu₂O/ZnO mixtures combined and their material loading is mentioned in the table 2. The electrodes prepared are dried in ambient conditions. Scanning electron microscope was used to characterize the electrodes.

Table 2: Material Loading and Compositions

Electrode	Cu ₂ O: ZnO ratio	Catalyst Loading, L, mg.cm ⁻²
Cu ₂ O	0.5: 0	0.5
Cu ₂ O	1:0	1
Cu ₂ O	2:0	2
Cu ₂ O-ZnO	1:1	0.5
Cu ₂ O-ZnO	1:0.5	1.5
Cu ₂ O-ZnO	1:1	2

The treated solid polymer membrane with the catalyst layers on each side were pressed at a slightly higher temperature for few minutes to acquire the electrode assembly and later cooled at room temperature. Figure 5 shows the arrangement of different layers and the other shows the actual membrane used. After finishing this step, the membrane is ready to be tested in the electrochemical cell.

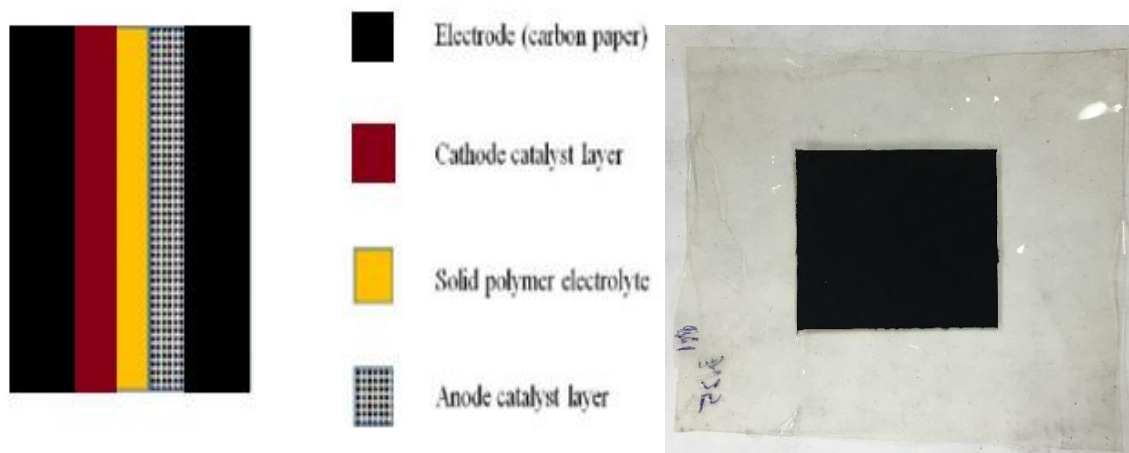


Fig 5: Layers of Solid Polymer Membrane (left), Snapshot of Actual Membrane (right)

3.4 Electrochemical Technique

The experimental measurements obtained during the electrochemical reduction of carbon dioxide were controlled by the potentiostat (PARSTAT 2273). The technique used here is linear sweep voltammetry and chronoamperometry process.

3.4.1 Linear Sweep Voltammetry

Linear sweep voltammetry is a method where the current present at the working electrode is observed, at the same time the potential between the reference and working electrode is graph linear in time. It provides fast and easy way to characterize a redox system. In this technique, the potentiostat assigns a linear sweep of computed potential range and audits the current as a function of applied voltage. Actually, this technique is observed using a straight analog ramp but because of the digitalized potentiostats the actual ramp includes series of small steps which gives the approximate linear ramp. In linear sweep voltammetry the voltage is scanned from a lower potential value to the higher potential value. As mentioned by the university of Cambridge, the slope of the line gives us the voltage scan rate (V). We can change the scan rate by altering the time taken. Linear

sweep voltammetry depends on series of factors such as rate of electron transfer, voltage scan rate and chemical reactivity of the catalyst. The current feedback is plotted as a function of time.

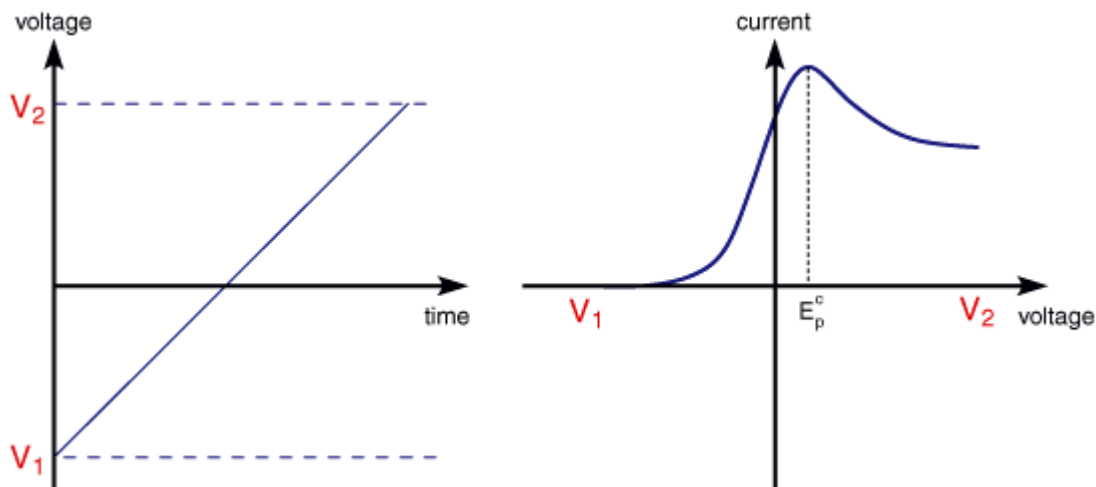


Fig 6: The linear sweep voltammetry measurement: (kla29@cam.ac.uk 2016) To the left is the potential-time profile given as an input while conducting the experiments, V_1 is the initial value and V_2 is the final value of our interest. To the right is the corresponding profile of the current due to shift in voltage values.

The scan starts from the left where there is no current flow. As the value of the voltage moves to the right the current flow increases and reaches a peak and starts dropping. Assumption that needs to be considered here is that the equilibrium voltage is applied at the electrode surface. The current continues to increase as the voltage moves from its initial value as the position of the equilibrium moves from left to right thus reducing the more reactants into products. But if the transfer of electron process is slower when compared with voltage scan rate then it is said that the reactions are irreversible electron transfer reactions. The main difference would be the position of maximum current depends on constant reduction rate and the scan rate. This is due to the fact that current

requires more time to react to the voltage applied on comparison with the reversible case.

3.4.2 Chronoamperometry

This technique works by keeping the potential constant and measuring the current as a function of time. For constant mode electrolysis, chronoamperometry technique is studied in electrochemical reduction of carbon dioxide. The electrons obtained from the reduction reactions accounts for the total charge and hence it corresponds to the amount of products formed. Over potential, which is the difference between the applied voltage and the attained equilibrium potential, which gives the additional required energy needed.

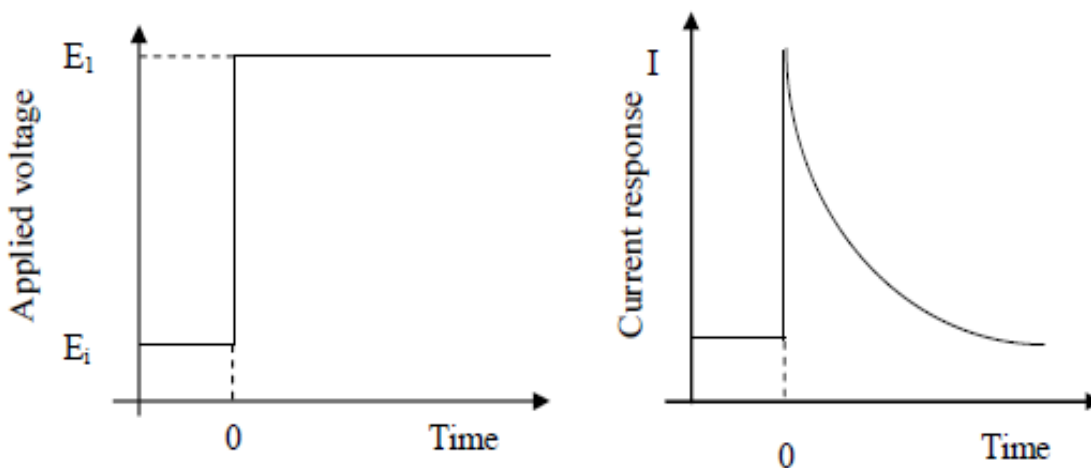


Fig 7: Chronoamperometric measurement. The voltage vs time profile to the left is the input given to the system during experiments where E_i is the initial value and E_1 is the final value. The current vs time plot to the right is the response obtained due to change in the voltage (Aeshala, Rahman, and Verma 2011). While conducting Chronoamperometric experiment the working electrode is maintained at E_i . When $t=0$, the voltage spontaneously reaches to different value E_1 . The current response recorded during this change in voltage values is shown in the figure. The total system charge is calculated by integrating current response which gives Faradaic efficiencies and total mole products.

4 CHARACTERIZATION METHODS

The solid polymer electrolyte membranes developed are allowed to characterize under ex-situ conditions like scanning electron microscope (SEM) and later were placed in the electrochemical reactor for in-situ conditions to analyze the performance for the electrochemical reduction of carbon dioxide.

4.1 Ex-situ Characterization Methods

Scanning electron microscope has been used to evaluate the ex-situ conditions of the treated solid polymer membranes. SEM makes use of the shorter wavelength of the electrons when compared to the visible light generally used in the optical microscope in order to get high resolution images. Figure 8 is the cross section diagram of the SEM column of Hitachi 3500.

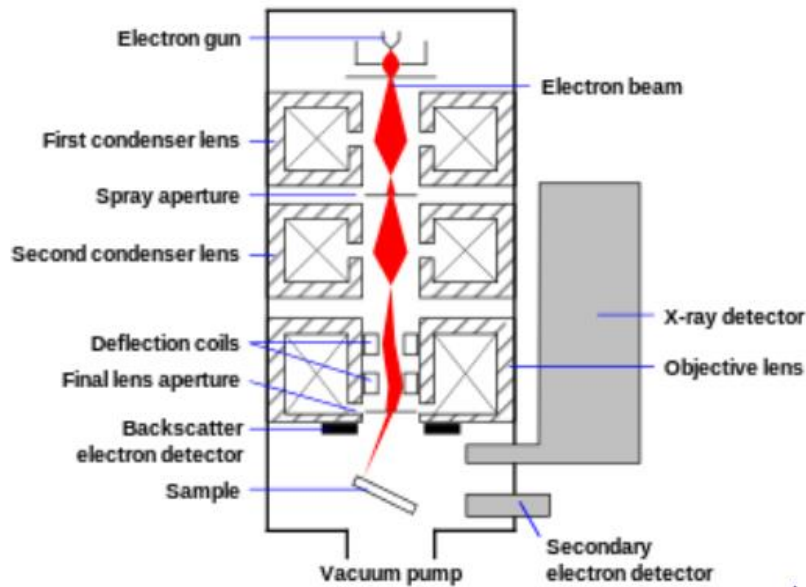


Fig 8: Cross Section of a Scanning Electron Microscope

The main components are depicted. The primary beam shape and collimation is created by the first condenser lens. The Gaussian shape beam is formed by grounding the stray

electrons with the help of the spray aperture. The electron beam again gets squeezed by the second condenser lens with a narrower Gaussian shape. The final focusing of the beam is done by the objective lens. The beam shape is minimized to stigmators with the help of deflection coils. The beam diameter is limited by the final aperture to reduce the beam divergence and to reduce the size of the spot.

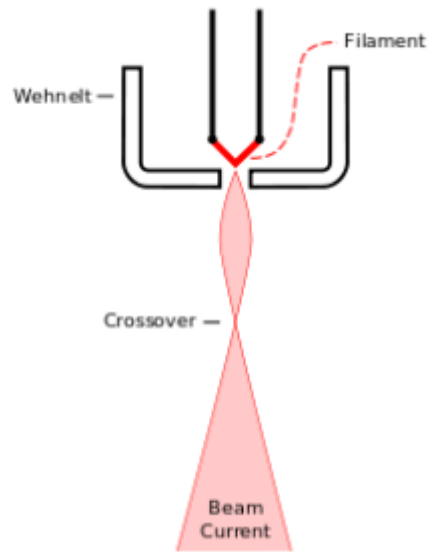


Fig 9: Working of Electron Gun in Scanning Electron Microscope

In the electron Gun, the electron source is called as Wehnelt Cylinder. The filament usually used is tungsten or LaB_6 and it gets heated by allowing current to flow. The current passed is directly proportional to the available beam current but upon heating the lifetime of the filament will be reduced. The Wehnelt cylinder is used to simulate a quasi-point source of electrons, and partially collimates the electron beam.

The morphologies of the surface of membranes are analyzed using SEM. The samples are mounted on a stub and are coated with graphite to make sure they are conducting for the analysis. The SEM images of the membranes to analyze the surface morphology of the copper oxide catalyst at different loadings as well as copper oxide and zinc oxide at

different ratios are shown below. The images are reprinted from J. Albo (Albo et al. 2015).

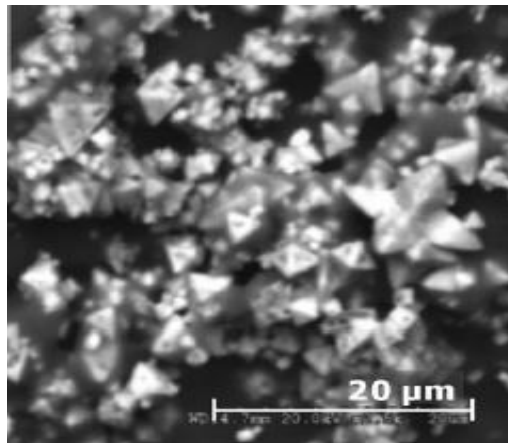


Figure 10: Scanning Electron Microscopy Image of Cu_2O $1\text{mg}/\text{cm}^2$ Loading

The catalyst was coated on a porous carbon paper which acts as a support to the catalyst. Figure 10 shows a tetragonal bipyramid morphology of the Cu_2O crystals having a particle size of $4\mu\text{m}$ which is more than the particle sizes disclosed for air oxidizes and cuprous oxide based electrodes which have $1\mu\text{m}$ and $2\mu\text{m}$ respectively.

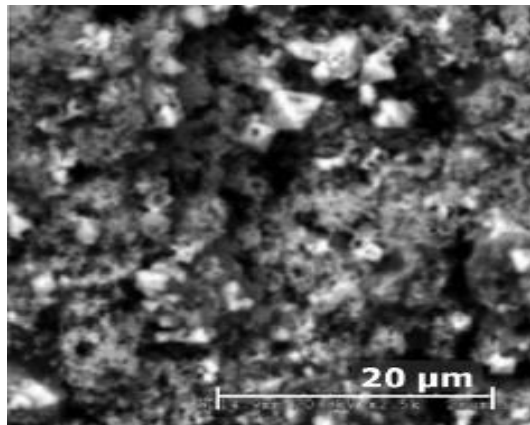


Figure 11: Scanning Electron Microscopy Image of $\text{Cu}_2\text{O}/\text{ZnO}$ (1:1), $2\text{mg}/\text{cm}^2$ Loading

Figure 11 shows a $\text{Cu}_2\text{O}/\text{ZnO}$ in 1:1 ratio sprayed on a supported carbon paper. The Cu_2O particles have the same tetragonal bipyramid morphology, but the particle sizes tend to be less than that of just Cu_2O particles.

For relative study, SEM images of Cu_2O at different loadings of 0.5, 1 and 1.8 mg/cm^2 are shown in figure 12, 13 and 14. The carbon paper is used as a support and thus forms the cathode. The copper oxide particles of different loadings are airbrushed on one side of the carbon paper as mentioned earlier. Different loadings are performed for the quantitative analysis to decide on the porosity of the cathode as the gaseous carbon dioxide transport which passes through the electrode. For optimization purpose different loadings of copper oxide was airbrushed on to the carbon support. In figure 12 and 13 we can see that the porosity of the carbon paper did not reduce much, whereas as shown in figure 14, when the loading was increased to 1.8 mg/cm^2 all of the carbon fiber strands are coated with copper oxide. It was inferred that as the agglomerate of copper increases the porosity of carbon support reduces.

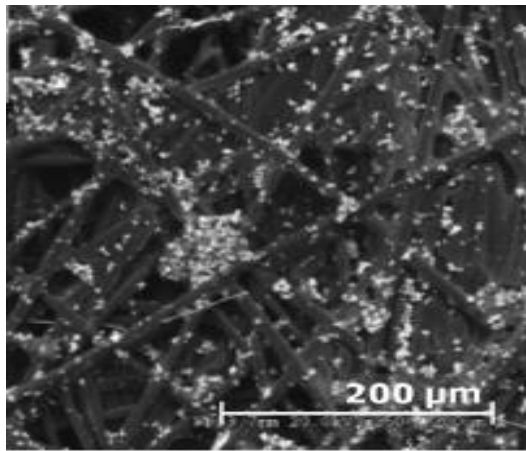


Fig 12: Scanning Electron Microscopy Image of Cu_2O 0.5 mg/cm^2 Loading

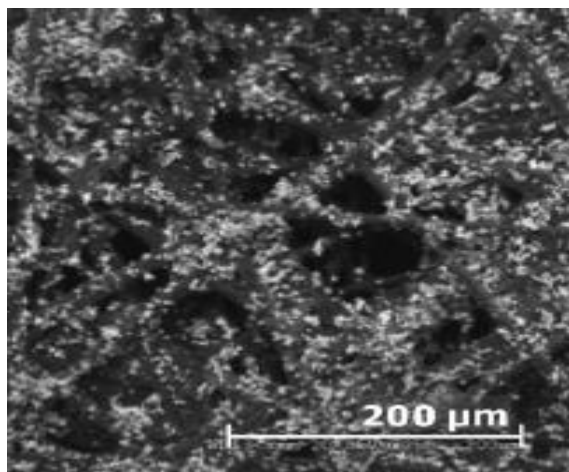


Fig 13: Scanning Electron Microscopy Image of Cu_2O $1\text{mg}/\text{cm}^2$ Loading

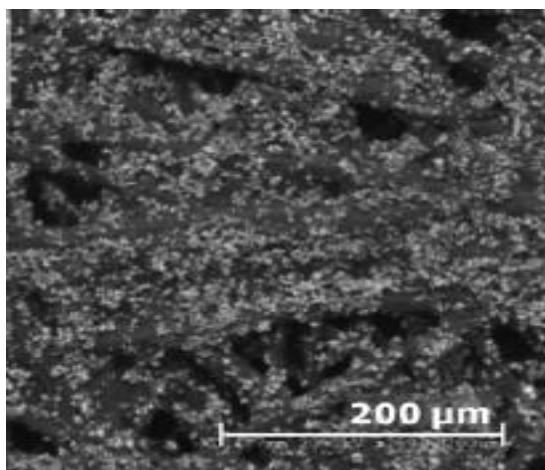


Figure 14: Scanning Electron Microscopy Image of Cu_2O $1.8\text{mg}/\text{cm}^2$ Loading

For relative study, SEM images of $\text{Cu}_2\text{O}/\text{ZnO}$ at 1:0.5, 1:1 and 1:2 ratios and loadings of $1.5\text{ mg}/\text{cm}^2$, $2\text{ mg}/\text{cm}^2$ and $3\text{ mg}/\text{cm}^2$ are shown in figure 15, 16 and 17. By observing these SEM images the $\text{Cu}_2\text{O}/\text{ZnO}$ particles are airbrushed and shows a uniformity in the Toray fibers. Jhong (Jhong, Ma, and Kenis 2013) has inferred that airbrushing the particles on to the carbon support the agglomeration of the catalyst minimizes. Due to this the electrodes are expected to perform with better catalytic activity due to the high surface to volume ratio, size, shape, surface composition (Andrews et al. 2013; Chang et

al. 2009b; Ohya et al. 2009). On comparing the $\text{Cu}_2\text{O}/\text{ZnO}$ with $1.5 \text{ mg}/\text{cm}^2$ loading with $2 \text{ mg}/\text{cm}^2$ there was not much of porosity change on the carbon support whereas when the loading was increased to $3 \text{ mg}/\text{cm}^2$ the carbon fibers are all coated with $\text{Cu}_2\text{O}/\text{ZnO}$ particles thus making it difficult for the gaseous carbon dioxide transport to the electrode surface. In order to optimize, different loadings were tested and it was noted that higher the loading, a compact layer is being formed thus reducing the porosity of the carbon support and also the performance of the electrode.

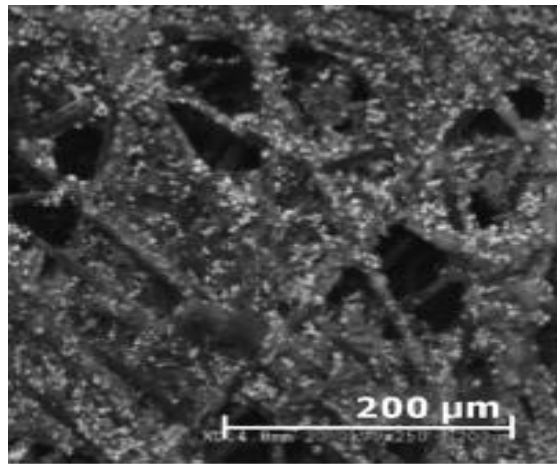


Figure 15: Scanning Electron Microscopy Image of $\text{Cu}_2\text{O}/\text{ZnO}$ (1:0.5), $1 \text{ mg}/\text{cm}^2$ Loading

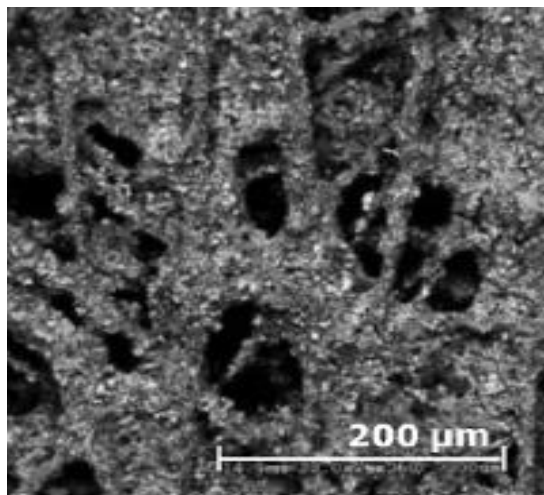


Figure 16: Scanning Electron Microscopy Image of $\text{Cu}_2\text{O}/\text{ZnO}$ (1:1), $2 \text{ mg}/\text{cm}^2$ Loading

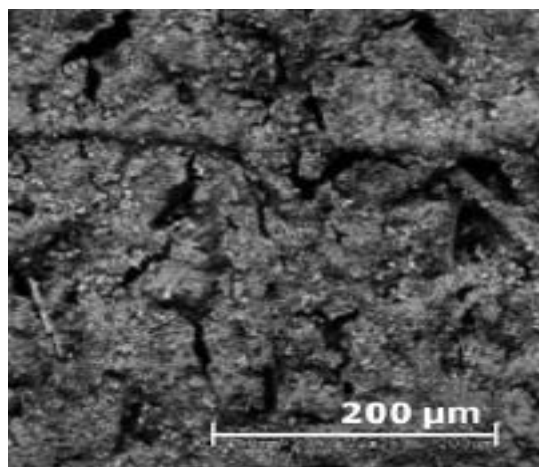


Figure 17: Scanning Electron Microscopy Image of $\text{Cu}_2\text{O}/\text{ZnO}$ (1:2), $3\text{mg}/\text{cm}^2$ Loading

4.2 In-situ Characterization Methods

After the solid polymer membranes are characterized using SEM, they are placed in the electrochemical reactor to obtain the in-situ characterization of the solid polymer membranes. The MEA was placed between the monopolar plates to analyze the performance of the electrochemical reactor. Figure 18 is the experimental setup for electrochemical reduction of carbon dioxide. As we can see from the figure the CO_2 gas which is 99.995% pure is taken from the cylinder with the help of a pressure regulator and is delivered at the cathode of the reactor with a flow rate of $20\text{ ml}\cdot\text{min}^{-1}$ adjusted by the rotameter. At the anode deionized water is fed with the help of a peristaltic pump at a flow rate of $1.5\text{ ml}\cdot\text{min}^{-1}$. MEA which is made up of stack of layers i.e. anode gas diffusion, anode catalyst, nafion membrane, cathode catalyst and cathode gas diffusion layer. The energy required to reduce the CO_2 is provided by the potentiostat- PARSTAT 2273. A range of potentials from 1.75 V to 3 V are given to the electrochemical reactor. Excess water is collected at the vent present on the anode, while cathode vent is connected to a liquid/gas separator which distinguishes between liquid and gas. The

outlet of this separator is connected to the tedlar bag, which collects the products obtained from reducing CO₂ and later injected into GC to test for hydrogen and carbon monoxide. The experiments were repeated while connecting the cathode vent to the RGA for qualitative analysis of the products obtained.

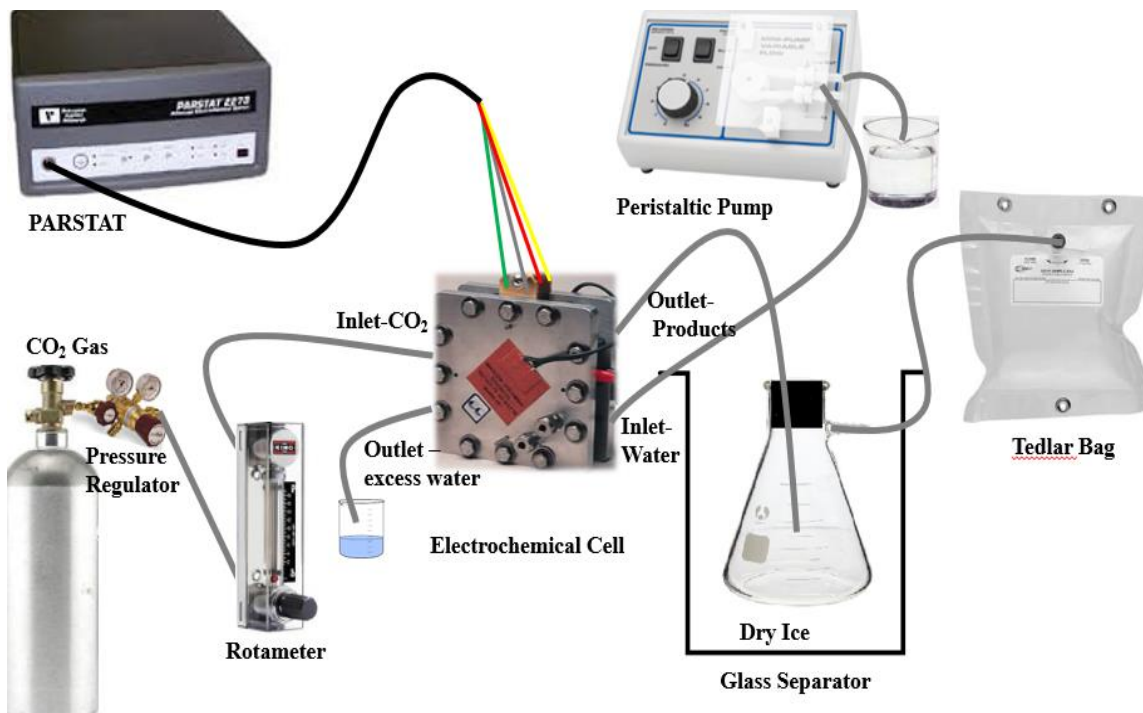


Fig 18: Pictorial Representation of Electrochemical Setup

All the experiments were performed at various temperatures ranging from 0°C to 40°C for about an hour. After every experiment the MEA's were replaced due to the degradation of the membrane. Linear sweep voltammetry technique which gives us the current vs voltage plots and chronoamperometry technique which keeps the potential constant and measures the current with respect to time, were used in analyzing the performance of the electrochemical reactor.

5 PRODUCT ANALYSIS

5.1 Gas Chromatography

Gas Chromatography is often used analytic technique to analyze the reaction products obtained from the electrochemical reactor. It is used in several research work as well as in industrial laboratories for quality control and to analyze and distinguish compounds in a mixture. The reaction products should be thermally stable and volatile to be tested by gas chromatography. In 2012 Kuhl (Kuhl et al. 2012) has reported that in the research of ERC, evaluation of the reaction products is one of the major challenges faced.

Firstly, products collected from the electrochemical cell are isolated by a liquid/gas separator before fed into the gas chromatography. Two phases are required for this technique- mobile and stationary. The mobile phase comprises of the carrier gas commonly inert gasses- helium, argon or nitrogen. The stationary phase dwells on packed column where the solid support itself acts as stationary phase or is coated with a high boiling polymer also called as liquid stationary phase. Usually, GC uses capillary columns, where the walls of the small diameter tube is directly coated by the stationary phase. The dimensions of the small diameter tube are 0.25 m film and 0.32 mm tube.

The mobile phase is allowed to pass through the column which is present in the stationary phase. The components of the sample merge with the stationary phase in the column and according to their strength they take long or short durations to flow along the column. Stronger the interaction between column and formed products the longer is the retention time, whereas weaker the interactions lead to shorter retention time. Column temperature and the flux of the carrier gas also has an effect on retention time. Depending on the strengths of interactions with the stationary phase the compounds get separated. There are

many factors which influence separation of the compounds (“Gas Chromatography” 2013).

1. Column temperature

As the temperature of the column increases the retention time decreases, i.e. high column temperature results in very short retention time. The main problem with high column temperatures is all components stay in gaseous phase thus leading to poor separation. On the other hand, for the separation to happen the compounds should be allowed to merge with the stationary phase. If they don't merge with the stationary phase, then it decreases the retention time. The quality of the separation decreases, because the distinctions in retention times are not noticeable anymore. The quality of separations is high for temperature gradients.

2. Boiling point

The boiling point of a compound and polarity are generally correlated as the compound will be in gas phase for most of the time. In order to mitigate this problem low boiling solvents are used to dissolve in the sample. They are principally diethyl ether, dichloromethane and so forth. The temperature of the column does not need to be over the boiling point because every compound has a non-zero vapor pressure at any temperature, including solids. That is the motivation behind why we can notice compounds like camphor (0.065 mmHg/25 °C), isoborneol (0.0035 mmHg/25 °C), naphthalene (0.084 mmHg/25 °C), etc. However, their vapor pressures are fairly low compared to liquids (i.e., water (24 mmHg/25 °C), ethyl acetate (95 mmHg/25 °C), diethyl ether (520mmHg/25 °C)).

3. The polarity of components versus the polarity of stationary phase on column

If the stationary phase and the compound share the same polarity, the retention time increases on the grounds that the compound and the stationary phase interaction becomes stronger. As a result, in polar stationary phases compounds have long retention times and in non-polar columns they have shorter retention times utilizing the same temperature. Chiral stationary phases that depend on amino acid derivatives, cyclodextrins and chiral silanes are equipped for isolating enantiomers since one enantiomer interacts slightly stronger than the other, due to steric effects or other particular interactions. For instance, a cyclodextrin column is utilized as a part of the determination of the enantiomeric overabundance in the chiral epoxidation experiment.

4. Carrier gas flow rate

A high flow rate diminishes retention times, as a result poor separation would be observed. As stated above, the components have very little time to collaborate with the stationary phase and are simply being pushed through the column.

5. Column length

A longer column generally enhances the separation. The exchange is that the retention time increases proportionally to the column length and a huge peak widening will be seen due to increase in longitudinal diffusion that takes place inside the column. One needs to remember that the gas molecules are not only moving in one direction but also sidewise and in reverse directions. This expanding is conversely corresponding to the flow rate. Expanding is additionally watched on account of the finite rate of mass transfer between the phases and in light of the fact that the molecules are taking distinctive ways through the column.

6. Amount of material infused

Ideally, the chromatogram displays peaks in a symmetric shape also called as Gaussian curve. If a lot of sample is injected, the peaks shows a significant tailing, which leads to poor separation. Most detectors are relatively sensitive and do not need a lot of material in order to produce a recognizable signal. Under standard conditions just 1-2 % of the compound infused into the injection port goes through the column as in most GC instruments are operated in split-mode to avoid overloading of the column and the detector. The split less mode might be utilized if the sample is extremely low in concentration.

Thus we can conclude that high temperatures and high flow rates decreases the retention time and additionally deteriorate the quality of the separation.

As the compound wash out from the column, they interact with the detector. This interaction gets converted into an electronic signal which is sent to the system. As a result, a chromatogram is generated which is plotted between magnitudes of the signal versus time calculated from the time of injection. Detectors are of different types based on their response to specific structures and functional groups. Some detectors acknowledge any solute coming from the column while others acknowledge only to solutes with specified structures and functional groups or atoms. Selective detectors are those detectors that acknowledges to specific types of solutes. Most detectors require one or more gases to function accurately. There are four different types of gasses, mainly combustion, reagent, auxiliary and makeup gases. In some cases, one gas may have various functions. The selection of detector gas is dependent on a particular detector and is mostly common among the GC manufacturers. The flow rates for various detectors

usually depend on the GC manufacturers. In order to reach the optimal sensitivity, selectivity and linear range for a detector standard flow rates should be followed.

i. Mass Spectrometer (GC/MS)

Numerous GC instruments are combined with a mass spectrometer. The GC separates the compounds whereas the mass spectrometer helps to identify the compounds depending on their fragmentation pattern.

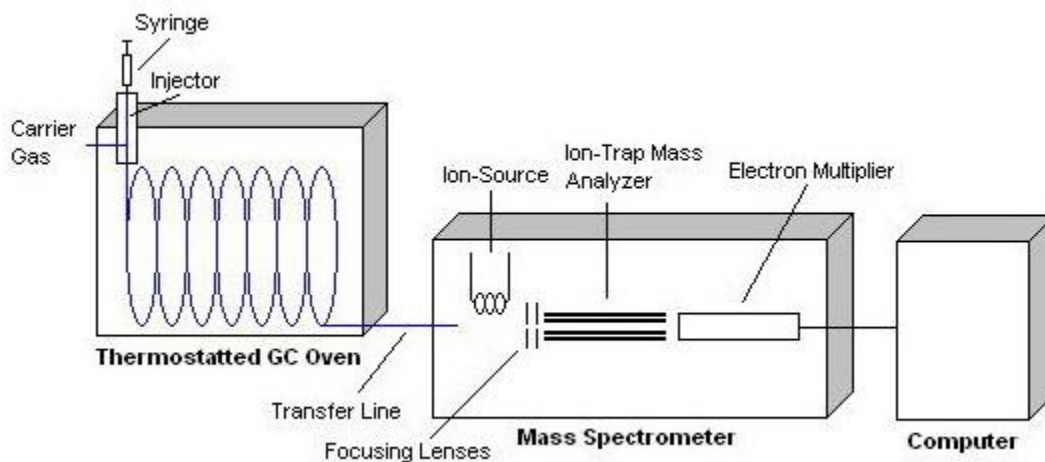


Fig 19: Illustration of GC/MS System

ii. Flame Ionization Detector (FID)

This detector is extremely sensitive towards organic molecules, yet relative insensitive for a couple of small molecules i.e., N_2 , NO_x , H_2S , CO , CO_2 , H_2O . If hydrogen and air are mixed in appropriate quantity, the combustion does not afford any ions giving a low background signal. If other carbon containing components, are introduced, cations will be produced so the more carbon atoms are in the molecule, the more fragments are formed and more is the sensitivity. Unfortunately, the quantity of carbon atoms and the size of the signal have no relationship. As a result, the individual response for each compound

must be experimentally determined for each instrument in order to avoid the pyrolysis of the sample, it is not suggestable for preparative GC. In addition, several gases are normally required to operate a FID: hydrogen, oxygen and a carrier gas or any compressed air.

iii. Thermal Conductivity Detector (TCD)

TCD detector is less sensitive than the FID (10^{-5} - 10^{-6} g/s, linear range: 10^3 - 10^4), yet is appropriate for preparative applications, because the sample is not destroyed. There are two gas streams, one containing only the carrier gas, the other one containing the carrier gas and the sample. The detection is based on these two gas streams. Usually, a carrier gas having high thermal conductivity i.e., helium or hydrogen is utilized to maximize the temperature difference between two filaments. The large surface-to-mass ratio allows a quick equilibration to a steady state. Wheatstone bridge circuit is used to observe the temperature difference between the reference and the sample cell filaments.

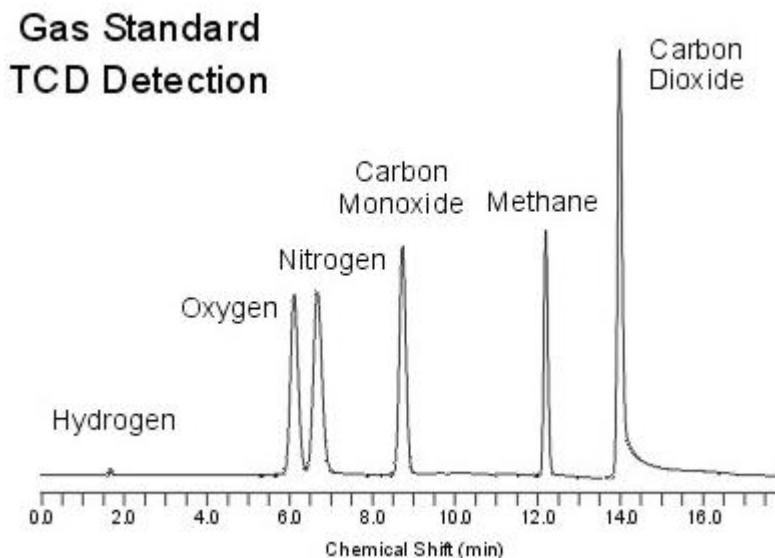


Fig 20: Standard Gas Chromatography detection for mixture of gases

Figure 20 depicts the standard gas chromatography by a TCD detector for various gasses.

Regardless the detector type, the x-axis remains to be the retention time and y axis is the amount of gasses absorbed or present. Retention times as well as peak heights are determined from this graph, thus chemical properties of the samples are determined.

iv. Electron Capture Detector (ECD)

This detector comprises of a cavity which comprises of two electrodes and a radiation source that discharges radiation (i.e., ^{63}Ni , ^3H). The collision between electrons and the carrier gas (methane and inert gas) produces a plasma-containing electrons and positive ions. If electronegative atoms are available in a compound, the negative ions will be captured from these electrons and the rate of electron collection will decrease. Compounds with atoms of high electron affinity i.e. 10^{-14} g/s is extremely sensitive and has a small linear range approximately of 10^2 - 10^3 . This detector is frequently used in the analysis of chlorinated compounds for which it exhibits a very high sensitivity.

Table 3: Summary of Gas Chromatography Detectors and their Detection Limits

Detector Type	Samples Accepted	Detection Limit
Mass Spectrometer	Any sample	0.25 to 100 pg.
Flame Ionization	Hydrocarbons	1 pg./s
Thermal Conductivity	Any sample	500 pg./ml
Electron Capture	Halogenated Hydrocarbons	5 fg/s
Photoionization	Vapor and gaseous compounds	0.002 to 0.02 $\mu\text{g/L}$

5.2 Residual Gas Analysis

Residual Gas Analyzer (RGA) is an equipment which measures the gasses at low pressure environment. RGA helps in analyzing the chemical species present in the

gaseous phase reactions and is useful in determining the important reactions. It also invigilates the stability of the gas and notices if there are any changes made while running the experiment. It is easy to find out if there is any leakage in the system or if the gas has been contaminated or mass flow controllers are out of calibration and this what makes RGA more convenient equipment. Operation of RGA is quite simple. Figure 21 gives detail description of how RGA operates.

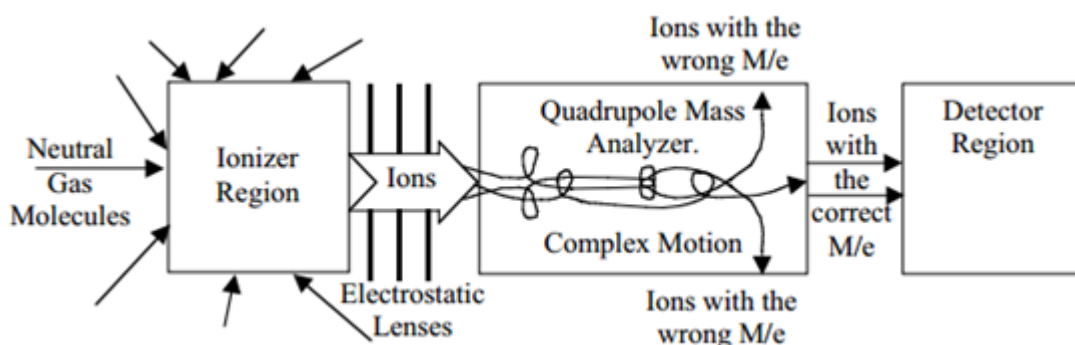


Fig 21: Layout of Residual Gas Analyzer

Photo Courtesy: (“Microsoft Word - Lab_7_RGAs.doc - Lab_7_RGAs.pdf” 2016)

The ionizer is responsible for converting neutral gas molecules to positive ions at specific electric potential. The electrostatic lenses accelerate these ions to transform into a beam of 20 eV energy. The role of Quadrupole mass analyzer is to act as a filter for the ions coming from the Ionizer region. The ions that match with the specified mass to charge ratio (M/e) are allowed to flow through it while the remaining ions which do not match with the specified mass to charge ratio are driven to the walls thus becoming neutral and undetectable. The mass to charge ratio and the measurement of the signal response will enable us to know the number of molecules that were present initially in the ionizer region. Analyzing the whole range of M/e ratios, it is easy to get the whole range of molecules present in the ionizer region which in turn gives the whole range of chemical

components present in the gas. So the analysis is made with the help of a spectrum as denoted in figure.

The amu on the x-axis refers to atomic mass unit whereas the y-axis refers to intensity or the mass of on proton.

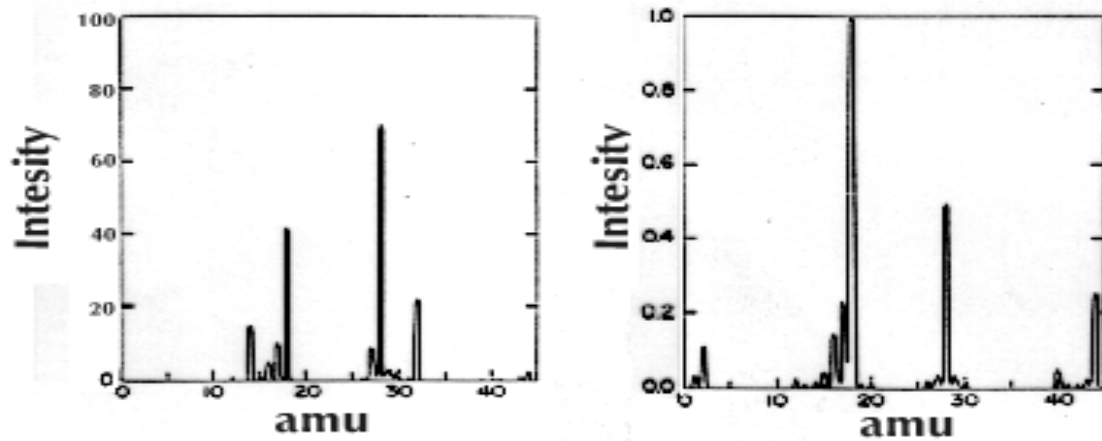


Fig 22: RGA Spectrum: The left spectrum was recorded then pressure reaches the RGA's working rang. The spectrum to right was recorded much later i.e. at lower pressure.

Photo Courtesy: ("Kurt J. Lesker Company | Simple RGA Spectra Interpretation | Vacuum Science Is Our Business" 2016)

6 RESULTS and DISCUSSIONS

6.1 Test Results Obtained Using Linear Sweep Voltammetry Technique

To examine the electrochemical behavior of prepared membranes as per section 3.3, the polarization response for different electrode membranes and loadings is calculated according to the procedure mentioned in 3.1 by using the technique discussed in section 3.4.1. The current densities were normalized to the area of the electrodes. The current-voltage curve for different electrodes has been plotted below. The polarization test was done at different temperatures from 25⁰ C, 30⁰ C, 35⁰ C and 40⁰C respectively with a flow rate of 20ml/sec of CO₂ and 15ml/sec H₂O.

E-Tek electrodes:

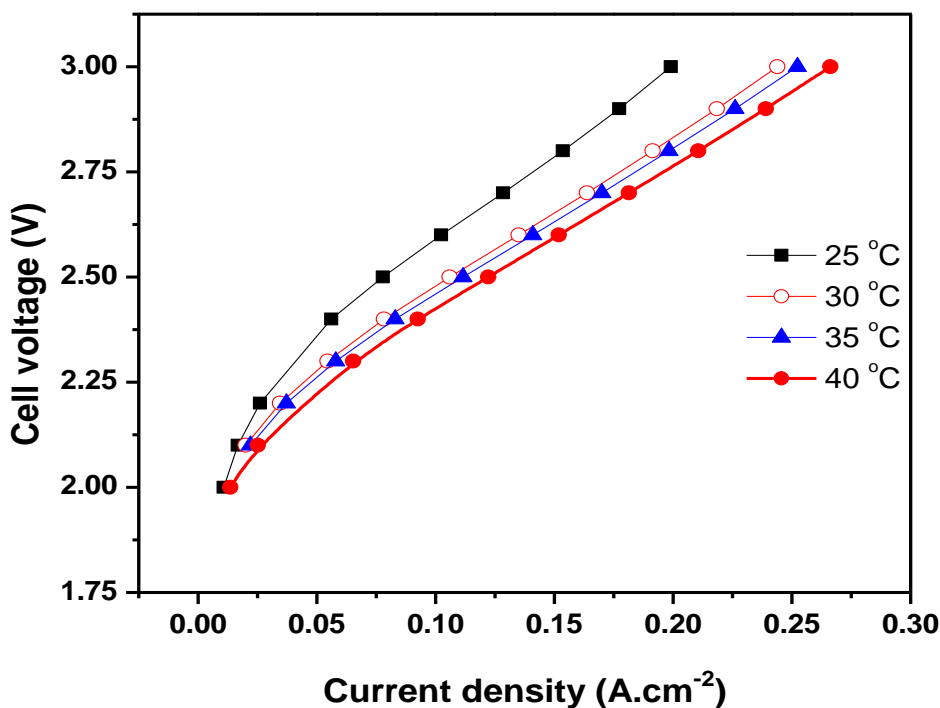


Fig 23: Platinum E-tek Electrodes for CO₂ Reduction Polarization Plot

The output of the electrochemical cell during testing is plotted above. The current density was better at 40⁰C when compared with other temperatures. As we carefully observe the

plot, as the temperature increases the performance of the solid polymer electrolyte i.e. nafion increases thus increasing the current density at the highest temperature.

Table 4: Polarization Results at Various Temperatures for E-Tek Electrodes

Temperature (°C)	Current Density (A.cm ⁻²)	Voltage (V)
25	0.1991	3
30	0.243	3
35	0.252	3
40	0.266	3

Platinum Coated Membrane:

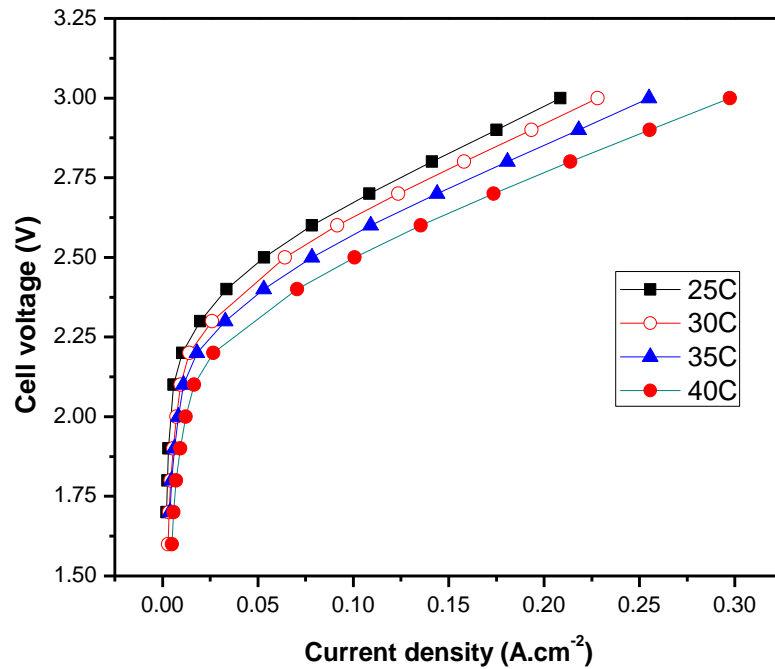


Fig 24: Platinum Coated Membrane for CO₂ Reduction Polarization Plot

The output of the electrochemical cell during testing is plotted above. The current density

was better at 40⁰C when compared with other temperatures. As we carefully observe the plot, as the temperature increases the performance of the solid polymer electrolyte i.e. nafion increases thus increasing the current density at the highest temperature. The coated platinum membrane gave better performance compared to that of commercial electrodes. These results were quite encouraging to continue further.

Table 5: Polarization Results at Various Temperatures for Platinum Catalyst

Temperature (°C)	Current Density (A.cm ⁻²)	Voltage (V)		
25	0.208	3		
30	0.228	3		
35	0.255	40	0.297	3
40	0.297	3		

Copper Oxide with 1 mg/cm² Loading:

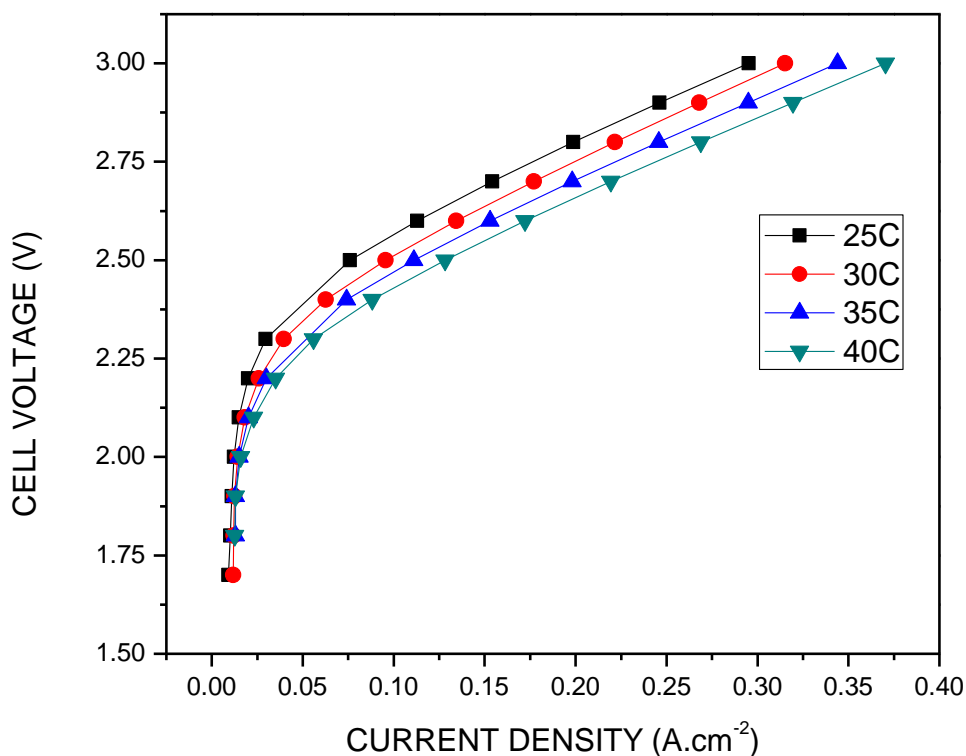


Fig 25: Cu₂O 1mg/cm² Membrane for CO₂ Reduction Polarization Plot

An oxidation-reduction contribution depends upon the catalytic loading. Nonetheless, the main feature of this plot is the reduction process, which starts around 2.15 V. The curve in the plot denotes the beginning of reduction process. It gave high current density at low voltage. The output looks promising.

Table 6: Polarization Results at Various Temperatures for Cu₂O 1mg/cm² Loading

Temperature (°C)	Current Density (A.cm ⁻²)	Voltage (V)
25	0.295	3
30	0.315	3
35	0.344	3
40	0.370	3

Copper Oxide with 2 mg/cm² Loading:

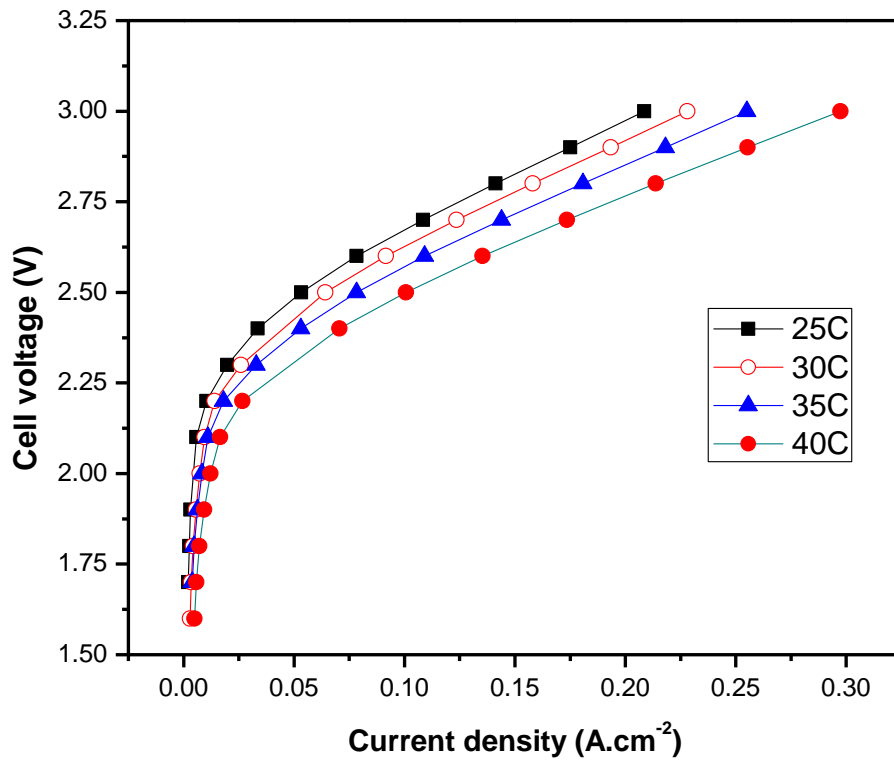


Fig 26: Cu₂O 2mg/cm² Membrane CO₂ Reduction Polarization Plot

The reduction process starts at 2.25 V a little later than that of copper oxide membrane with 1mg loading. It was observed that as the loading increases the performance of the membrane decreases. The optimum loading that found out was to be 1mg, while 0.5 mg loading was also experiments but the results were very poor. The main disadvantage with the copper oxide catalyst was the stability. It was observed that the performance of the catalyst degrades at longer times. It was due to the fact that at longer times metal particles detach from the nafion surfaces. In order to enhance the copper oxide electrodes inclusion of zinc oxide has been introduced.

Table 7: Polarization Results at Various Temperatures for Cu₂O 2mg/cm² Loading

Temperature (°C)	Current Density (A.cm ⁻²)	Voltage (V)
25	0.208	3
30	0.228	3
35	0.255	3
40	0.297	3

Copper Oxide – Zinc Oxide (1:1) with 1 mg/cm² Loading:

The copper oxide and zinc oxide loading were each 0.5 mg/cm². The performance of Cu₂O with 0.5 mg found to be very poor, but with inclusive of ZnO the performance enhanced but it is still low. The advantage of adding ZnO was the durability of the electrode, stayed for longer retention times. As we can infer from the plot, the reduction process starts at different voltages at different times which was not in the case of copper oxide alone. It still continues to perform better at higher temperatures.

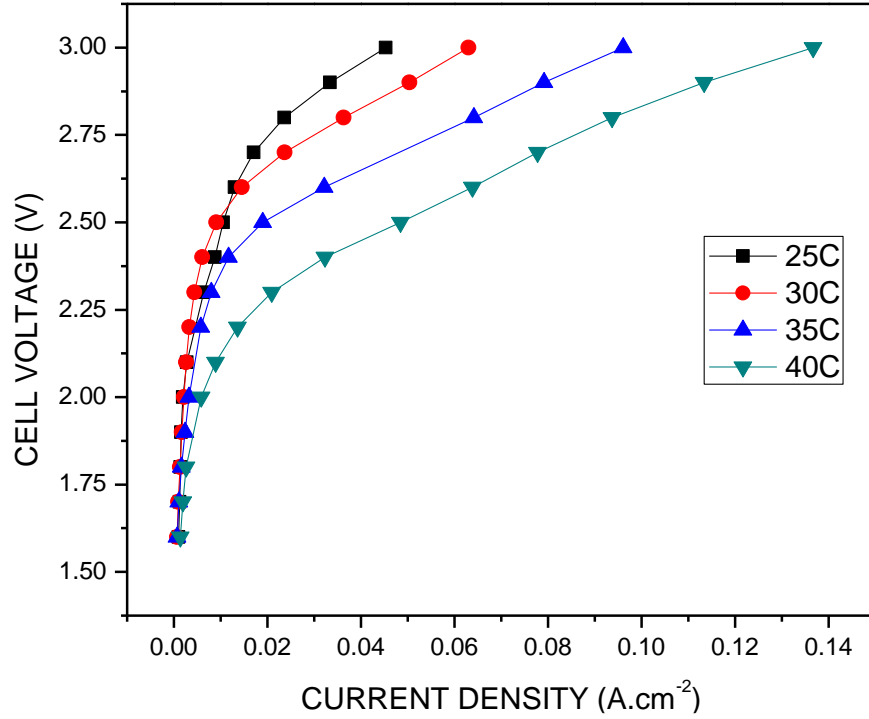


Fig 27: Cu₂O/ZnO (1:1) 1mg/cm² Membrane for CO₂ Reduction Polarization Plot

Table 8: Polarization Results at Various Temperatures for Cu₂O/ZnO (1:1) 1mg Loading

Temperature (°C)	Current Density (A.cm ⁻²)	Voltage (V)
25	0.045	3
30	0.063	3
35	0.096	3
40	0.136	3

Copper Oxide – Zinc Oxide (1:0.5) with 1.05 mg/cm² Loading:

The performance improved compared to Cu₂O-ZnO 1mg loading. But the maximum current density it reached was much lower compared to copper oxide 1mg loading. The reduction process started quite early at 1.875 V. The polarization response was very poor when the experiment was conducted at room temperature, improved when heated 40⁰C.

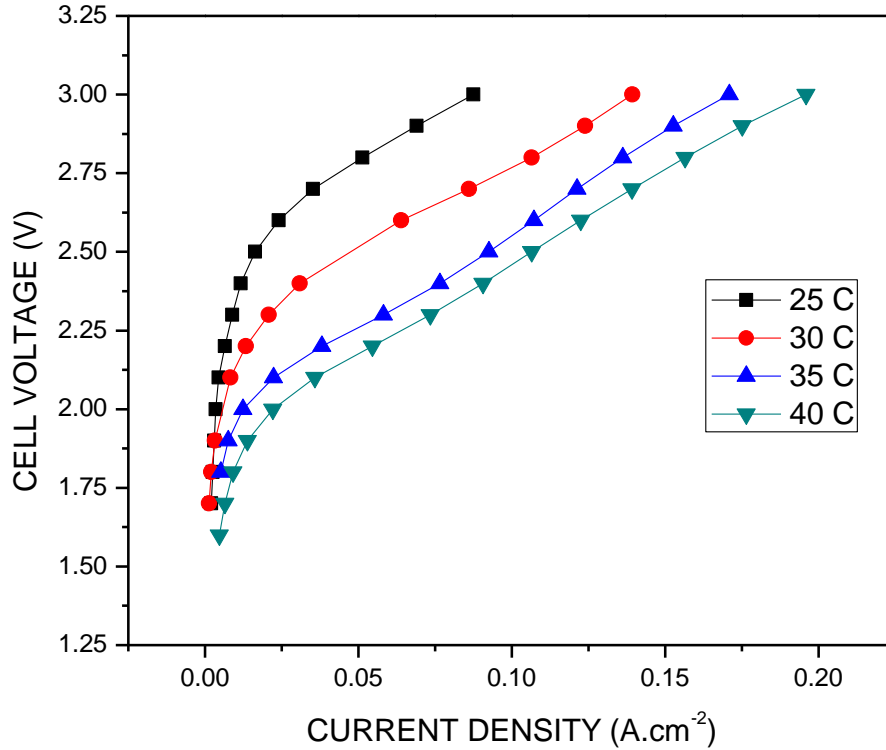


Fig 28: Cu₂O/ZnO (1:0.5) 1.5mg/cm² Membrane for CO₂ Reduction Polarization Plot

Table9: Polarization Results at Various Temperatures Cu₂O/ZnO (1:0.5) 1.5mg Loading

Temperature (°C)	Current Density (A.cm ⁻²)	Voltage (V)
25	0.087	3
30	0.139	3
35	0.170	3
40	0.195	3

Copper Oxide – Zinc Oxide (1:1) with 2 mg/cm² Loading:

This membrane showed better performance compared to the Cu₂O-ZnO 1mg/cm² loading while less than that of Cu₂O- ZnO 1.5 mg/cm². The reduction process started little later at 2V. There was not much difference in the polarization response for 25⁰C and 30⁰C, but

we can notice there is a huge jump when the membrane heated to 40⁰C. It is inferred that Cu₂O- ZnO 1.5 mg/cm² membrane gives better performance when heated to higher temperature. It is because of the fact that higher the applied voltages greater would be the reaction kinetics.

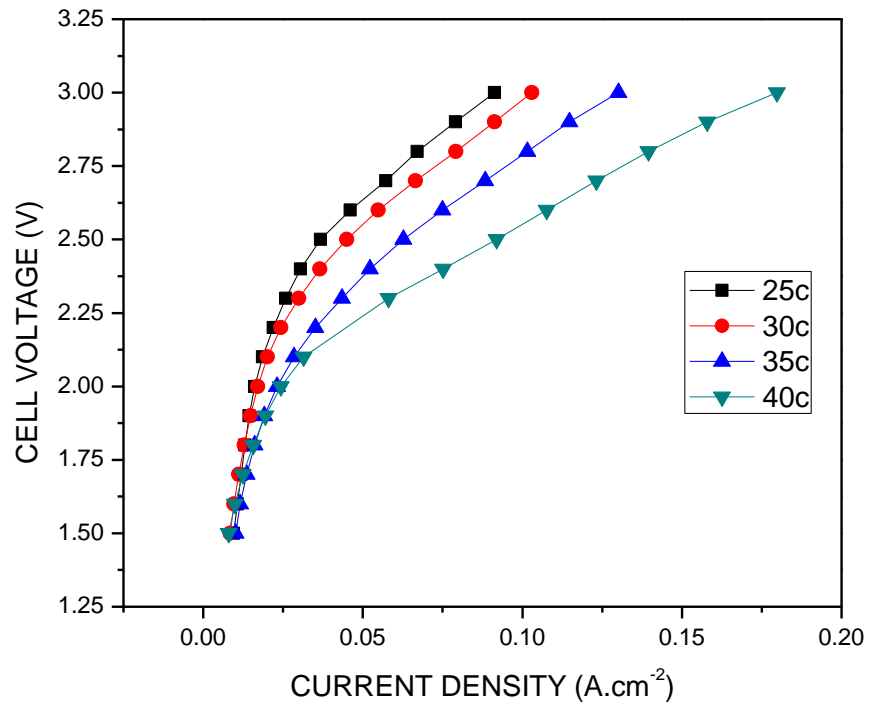


Fig 29: Cu₂O/ZnO (1:1) 2mg/cm² Membrane for CO₂ Reduction Polarization Plot

Table 10: Polarization Results at Various Temperatures Cu₂O/ZnO (1:1) 2mg Loading

Temperature (°C)	Current Density (A.cm ⁻²)	Voltage (V)
25	0.091	3
30	0.103	3
35	0.130	3
40	0.179	3

Lanthanum Copper Oxide:

This material was introduced newly into this topic. The main advantage of this material is they behave as conductors at very high temperatures, this enables to produce good results. But the preliminary experiments were not so encouraging further research has to be done regarding this material.

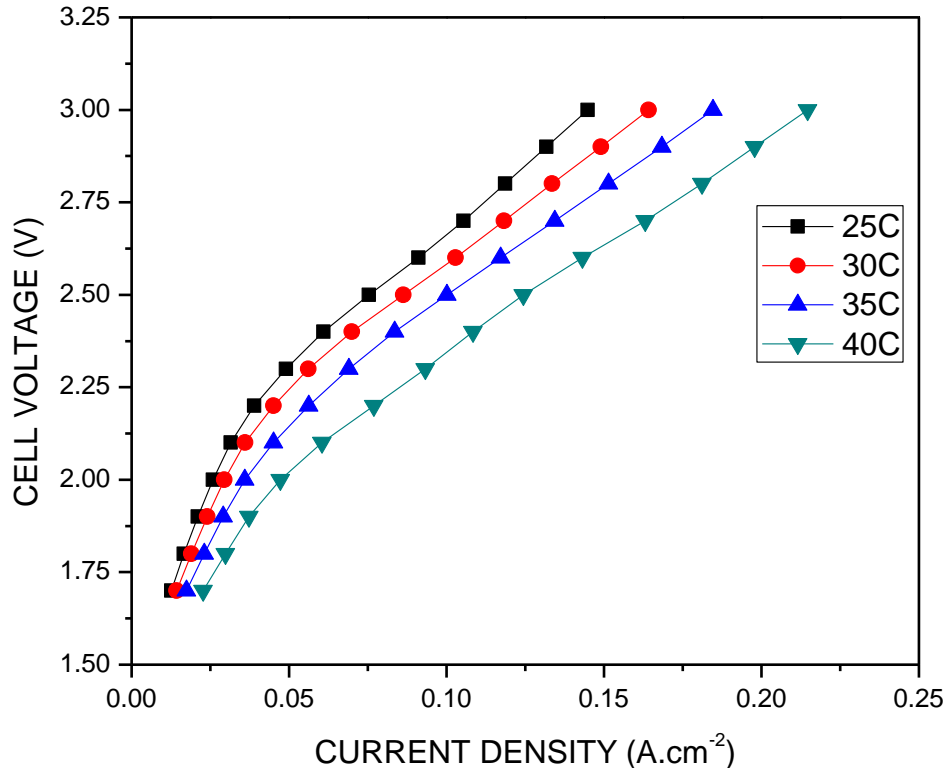


Fig 30: La₂CuO₄ 2mg/cm² Membrane for CO₂ Reduction Polarization Plot

Table 11: Polarization Results at Various Temperatures for La₂CuO₄ 2mg Loading

Temperature (°C)	Current Density (A.cm ⁻²)	Voltage (V)
25	0.144	3
30	0.164	3
35	0.184	3
40	0.214	3

Comparison of all the Material Performance:

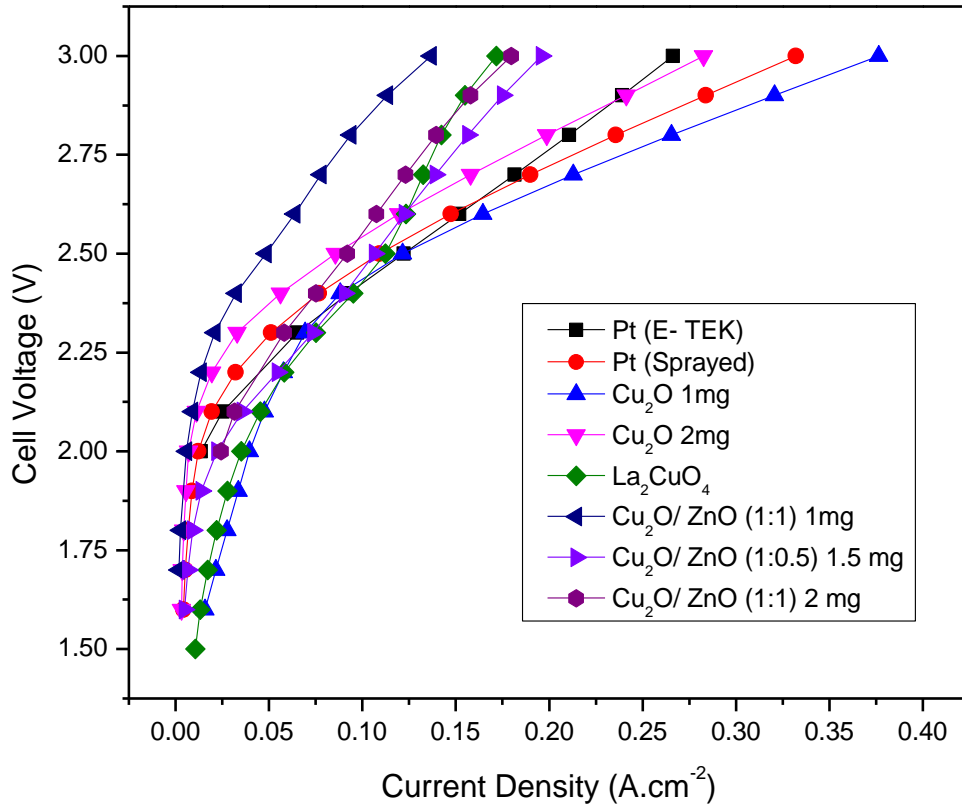


Fig 31: Polarization Curves for all Materials at 40°C and 3V for ERC

Above is the plot of polarization curves for all the catalyst materials maintained at 40°C. On comparing all the individual plots, it was observed that the membrane performance was excellent at 40°C. From the figure 31, we can draw a conclusion that the best performance was obtained with Cu₂O 1mg loading with a current density of about 0.376 A.cm⁻² and the least performed membrane was Cu₂O-ZnO (1:1) with 1mg/cm² loading. This membrane has marked current density of 0.136 A.cm⁻² at 40°C.

Table 12: Polarization Results of Various Materials, Loadings Maintained at 40⁰C 3V

Electrode	Cu ₂ O: ZnO weight ratio	Catalytic Loading (mg.cm ²)	Current Density (A.cm ⁻²)
Cu ₂ O	1:0	1	0.376
Platinum	-	1	0.331
E-Tek	-	1	0.266
Cu ₂ O	1:0	2	0.282
Cu ₂ O-ZnO	1:0.5	1.5	0.195
Cu ₂ O-ZnO	1:1	2	0.179
La ₂ CuO ₄	-	2	0.171
Cu ₂ O-ZnO	1:1	1	0.136

6.2 Performance Evaluation of ERC using GC

Various products are obtained by feeding gaseous CO₂ into the electrochemical cell at voltages upto 3V observed by GC. The GC instrument is equipped with TCD detector which helps in detecting only H₂ and CO. As we have seen in section 6.1 the current density increases as the applied voltage increases which implies that the rate of reactions is also directly proportional to the applied voltage. Increase in rate of charge means that there is increase in charge absorbed by the chemical reactions at the electrode surface. So the marked current density leads to formation of products like H₂ and CO. The interesting factor here is platinum produces more hydrogen than Cu₂O with 1mg loading. But we have observed that Cu₂O with 1mg loading produced higher current density compared to platinum. So we can draw an inference that there were other gasses present when tested with Cu₂O with 1mg loading membrane which cannot be detected by the GC. Hence

RGA has been introduced to perform the quantitative analysis and to understand the hydrocarbons present in the output.

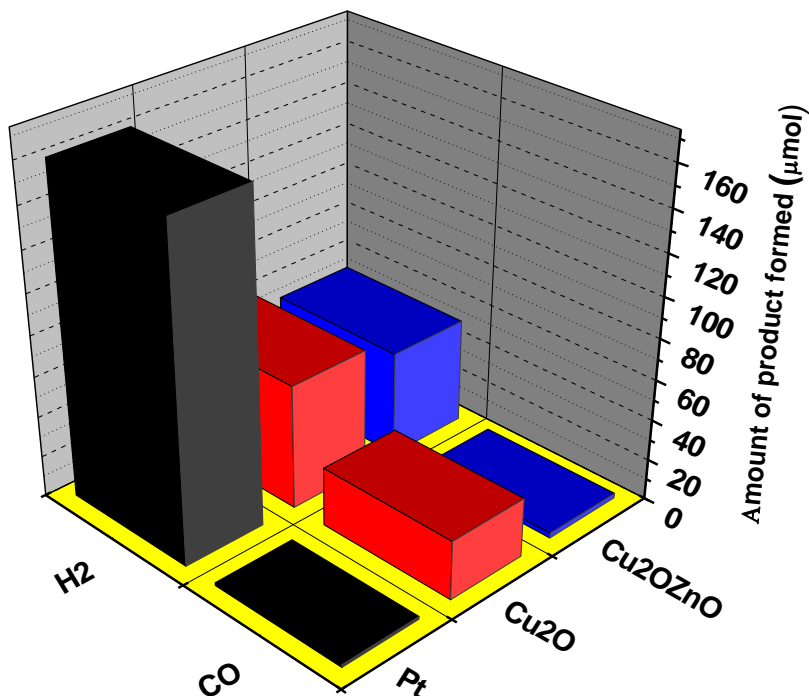


Fig 32: Amount of Products Formed for Various Materials

Coming back to the data plotted above, it was observed that the hydrogen production increases with the increase in current density at any mentioned voltage. Except hydrogen the remaining products decrease after a certain voltage whereas H₂ production pattern is similar to that of current density. During the electrochemical reduction of CO₂ most of the energy is used for H₂ production when compared with the other products formed. Platinum produces 1.41 μmol of CO and 161.084 μmol of H₂. This clearly states that the voltage applied was mainly used for H₂ generation. It might be due to proton and electron

transfer which occurred mostly at high voltages.

Faradaic efficiency is a crucial criterion to explain the concept of electrochemical reduction of CO₂ selectivity (Jhong, Ma, and Kenis 2013). The products obtained are hydrogen and carbon monoxide with faradaic efficiencies of 8.98% for platinum, 10.91% for Cu₂O-ZnO weight ratio 1:0.5 with 1.5mg/cm² loading and 9.66% for Cu₂O 1mg loading at current densities of 0.331 A.cm⁻², 0.376 A.cm⁻² and 0.195 A.cm⁻² respectively.

6.3 Performance Evaluation of ERC using RGA

RGA illustrates the data obtained for the electrochemical reduction of carbon dioxide. The scan rate is plotted against the signal intensity which determines the molecular weight of the gas. The procedure for testing the catalyst in RGA is already discussed in section 5.2. We initially record data in the form of histogram for every scan number, which enables us to know at what molecular ratio the peak is being formed. So, by combining all the scan rates and all the peaks we can identify the change in peaks and their pattern which helps us on identifying the particular gas.

Figure 33, is the signal intensity Vs scan rate plot for the electrochemical reduction of CO₂. The main products that was identified was hydrogen. Similar to what has been identified by GC. On observing the plot, we can see that there is a change in the black line denoted for H₂ whose molecular weight is 2 is because the experiment was conducted at different voltages. The first step up we can see in the plot is because the voltage was increase to 2V and the second step up in the plot is due to increase in voltage from 2V to 3V. It can be concluded that the main product that is formed when tested with platinum catalyst is H₂.

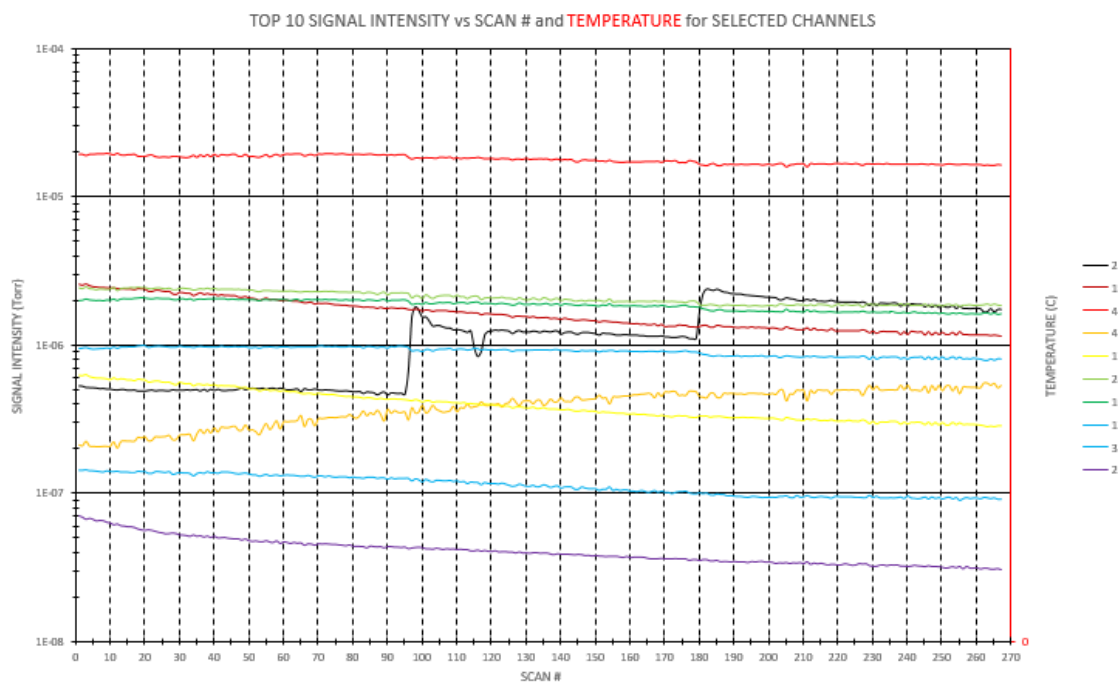


Fig 33: Signal Intensity Vs Scan Rate Plotted for Reduction of CO₂ using Pt Catalyst

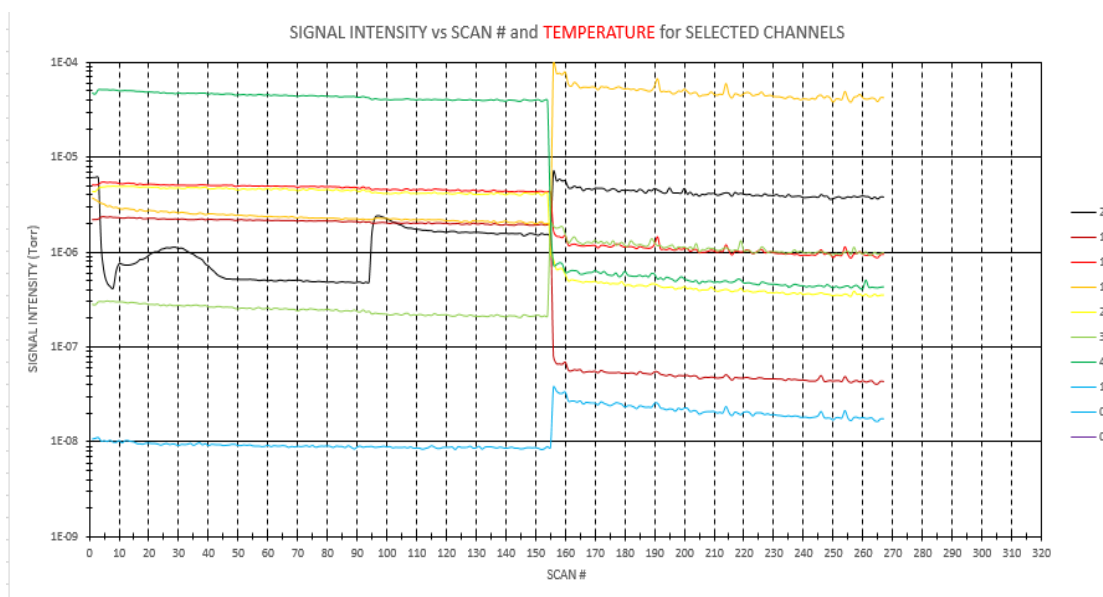


Fig 34: Signal Intensity Vs Scan Rate Plotted for Reduction of CO₂ using Cu₂O Catalyst

Figure 34, depicts the signal intensity vs scan rate for electrochemical reduction of CO₂ using copper oxide with 1mg loading. It is noticed that when the voltage was increased to 2V there was shift in only product depicting hydrogen. The step up in the figure describes

that there was hydrogen. When the voltage was increased to 3V, we could see change in peak for hydrocarbons such as methanol and methane. The methanol having molecular weight of 32 has taken a significant step when the voltage was increase to 3V, thus indicating its presence in the output products. However, methane whose molecular weight is 16 has increased exactly at 3V but dropped immediately, the reason is unknown yet. Carbon monoxide having 2 as its molecular weight has taken a huge leap after 3V, thus indicating its presence. The important factor we need to look at here is the fall of CO₂ whose molecular weight is 44, has drastically dropped after applying 3V because of the generation H₂, CO, CH₃OH, CH₄ simultaneously.

7 CONCLUSION

7.1 Overview

In this study various catalysts were synthesized and characterized for the electrochemical reduction of CO₂ using solid polymer electrolyte. The exploration was principally centered on the improvement and investigation of the reactant items acquired from electrochemical reactor for ceaseless electrochemical diminishment of carbon dioxide in gas stage utilizing strong polymer electrolytes. The metal catalysts were sprayed on solid polymer electrolyte i.e. nafion and characterization was studied. The exploration was essentially done utilizing copper oxide at the cathode.

The anode and cathode were readied utilizing Pt/C and copper oxide respectively to frame a layer terminal get together. The reactor was produced effectively and the preparatory study demonstrates empowering results for ceaseless gas stage diminishment of CO₂. SEM pictures of the layers seem uniform without development of pores and cracks. Warm strength of the layers was likewise assessed as the films encounter high temperatures of around 110⁰C amid the creation of layer terminal gathering. Catalysts to be specific La₂CuO₄ experienced even high temperatures and were discovered stable.

Hydrogen and carbon monoxide were analyzed using Gas Chromatography with TCD detector. The faradaic efficiency obtained was 8.98% with platinum as a catalyst with current density as high as 0.2974 A.cm⁻², 10.91% with Cu₂O- ZnO in 1:0.5 molecular weight ratio with 1.5mg loading having current density equal to 0.195 A.cm⁻² and 9.66% with Cu₂O 1mg loading with a current density of 0.376 A.cm⁻² which was recorded as the highest among all the other materials testes in the electrochemical cell. At higher potentials, the connected voltage was basically used for hydrogen advancement, which

was in rivalry with CO₂ decrease response because of higher response energy. Also, bringing down potential was discovered towards the formation of other major products.

In this way the study satisfies the point of the examination work alongside the target. It might be noticed that selectivity of the items expanded yet at the same time need changes in the faradaic effectiveness. Nonetheless, to further make the durable and effective catalysts, some further extension alongside future bearing of the exploration is appeared in the following area.

7.2 Future Scope

Several questions are still need to be answered regarding electrochemical reduction of carbon dioxide method to attain extensive use. Studies should be done on improving the stability of the solid polymer electrolyte to enhance the performance of ERC. Research also has to be done on different catalyst materials and their lifetime. In addition, driving the whole process under the renewable energy like solar energy would allow us to achieve carbon neutral fuels or various other chemicals that are commonly obtained from petroleum. This technology of reducing carbon dioxide to a useful product using solid polymer electrolyte coupled with renewable energy source will undoubtedly become practical and economically feasible in the near future.

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